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CHEMICAL

REPORTS AND MEMOIRS,

ON ATOMIC VOLUME; ISOMORPHISM; ENDOSMOSIS;
THE SIMULTANEOUS CONTRAST OF COLOURS;
THE LATENT HEAT OF STEAM AT DIFFERENT PRESSURES;
THE ARTIFICIAL FORMATION OF ALKALOIDS;
AND VOLCANIC PHENOMENA.

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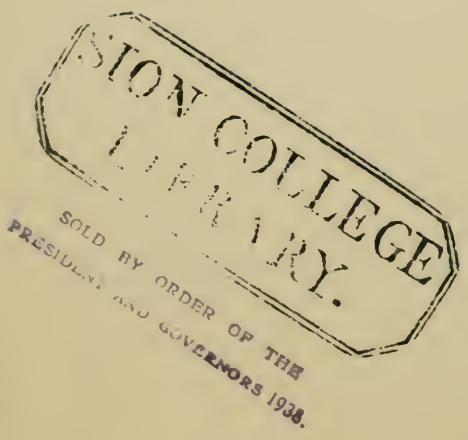
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PREFACE.

The First and Fourth Reports on Atomic Volume and Isomorphism, by Professor Otto, of Brunswick, contained in the present volume, are extracted from the second edition of that author's systematic work on Chemistry, now in course of publication*. They contain, I believe, a more detailed account of the researches and speculations of H. Kopp, Schröder, Löwig, and others, than has hitherto been given to the public. The imperfect but advancing state of these branches renders their critical discussion useful and opportune, and incites to farther inquiry. The more recent memoir of M. Filhol, translated from the *Annales de Chimie et de Physique*, t. xxi (*3me série*), has been added, as it contains a series of new determinations of the specific gravity of many substances, by which he is enabled to test M. Kopp's theoretical conclusions, and to modify them in several points.

The Report on Endosmosis, by Dr. Julius Vogel of Giessen, is the translation of a tract published separately by him, under the title of the report. The attention of chemists and physiologists has lately been recalled to this subject by the researches of Liebig on the Motion of the Juices in the Animal Body.

The Physical Investigations on Dyeing, by M. Chevreul, which form the fifth Memoir, were read before the French Academy, and published in the *Revue Scientifique et Industrielle*, t. xii., 1847, from which they have been extracted.

The valuable memoir of M. Regnault, On the Latent Heat of Steam at different Pressures, is a portion of a series of investigations undertaken by that chemist, at the instance of

* Lehrbuch der Chemie. Zum Theil auf Grundlage von Dr. Thomas Graham's *Elements of Chemistry*, bearbeitet von Dr. Fr. Jul. Otto, Ordentlichem Professor der Chemie am Collegio Carolino zu Braunschweig.

the French Government, to elucidate the theory of the Steam-Engine. It is extracted from a volume entitled, *Relation des Expériences entreprises par ordre de Monsieur le Ministre des Travaux Publics, et sur la proposition de la Commission Centrale des Machines à Vapeur, pour déterminer les principales lois et les données numériques qui entrent dans le calcul des Machines à Vapeur. Par M. V. Regnault, Ingénieur au Corps Royal des Mines, Membre de l'Academie des Sciences. Paris, Firmin-Didot,* 1847. This is a volume of the Memoirs of the French Academy, which has been published separately, and is accompanied by an Atlas of magnificent plates.

The report by Professor E. Kop, of Strasburg, on the Artificial Formation of Alkaloids, is also drawn from the *Revue Scientifique et Industrielle,* t. xi., p. 273.

The memoir by Professor Bunsen, on the Pseudo-Volcanic Phenomena of Iceland, was originally published in Liebig's *Annalen der Chemie und Pharmacie,* bd. lxii., 1847. It contains the new theory of the Irruptions of the Geyser Springs, established by M. Descloizeaux and the Author, with many interesting observations on the metamorphism of the palagonite rock, and other chemical changes observed in course of progress at this focus of volcanic activity.

The translation of all these papers has been executed by Dr. G. E. Day.

London, *July,* 1848. T. G.

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REPORT.

ON THE RELATION OF THE VOLUMES OF BODIES IN THE SOLID STATE TO THEIR EQUIVALENTS OR ATOMIC WEIGHTS.

By PROFESSOR OTTO, *of Brunswick.*

CHEMISTS fully comprehend the nature of the relation which exists between the equivalent of a substance and its volume in the gaseous state. Equal volumes of different gases or vapours do not always correspond to the same number of equivalents; or, if we may use the expression, the equivalents of different substances, when gasified, do not all fill an equally large space, and hence the equivalent volumes of gases and vapours are of different size. These gaseous volumes, however, always bear to each other a simple ratio, such as 1 to 2, 1 to 4, &c., and the difference is subject to known laws.

If we assume that the equivalent weights correctly represent the weight of the atoms of bodies, what has been said of the volume of the equivalents will apply to the volume of atoms in the gaseous state.

We are now in a position to consider whether the equivalents or atoms of bodies in the solid and fluid state occupy equal spaces, or spaces of different dimensions; whether the equivalent volumes or atom volumes of solid bodies are of the same or different sizes. The equivalent weights give the relations of weight in which bodies unite to form chemical compounds. If, now, we know the specific weights of bodies, we may determine the relation of volume in which they combine; for we have only to divide the equivalent weights by the specific weights in order to obtain a quotient expressing the relations of their volumes. Sulphur and zinc, for instance, combine chemically in the proportion by weight of 200 of the former to 406 of the latter; these numbers express the relation of their equivalent

weights. The specific weight of sulphur is 1·99, and that of zinc is 6·95; the relation of volume of these quantities of sulphur and zinc is therefore $\frac{200}{1·99}$ to $\frac{406}{9·56}$, or as 100 to 58; that is to say, 100 volumes of sulphur combine with 58 of zinc. Hence the quotients obtained by dividing the equivalent weights by the specific gravities express the relative volumes which the equivalents of bodies in the solid or fluid condition occupy; they are the equivalent volumes of solid and fluid bodies. If A designates the equivalent weight, and S the specific weight, then the equivalent volume is equal to $\frac{A}{S}$. To this quotient Kopp applies the term *specific volume*, since it is a relative number, like the specific gravity. But as the equivalent weights are relative numbers, and we cannot alter their designation to specific combining weights, I regard the term *equivalent volume* as a more suitable one, especially as it has been adopted in a corresponding sense for gases and vapours. If, instead of *equivalents*, we speak of *atoms*, the term *equivalent volume* becomes naturally converted into *atom volume*, a word which I first find used by Dumas, in this sense, in his *Traité de Chimie appliquée aux Arts*. Schröder, who, together with Kopp, has devoted much attention to this subject, has recently, at the suggestion of Berzelius, employed the term *molecular volume* in place of *equivalent volume*. In the illustration we have given, 100 is the equivalent volume of sulphur, and 58 that of zinc. The equivalent weight of nitrate of silver, AgO, NO_5, being 2125, and its specific weight 4·36, its equivalent volume is, therefore, $\frac{2125}{4·36}$ or 478.

It will be more clearly seen what we are to understand by the numbers indicating the equivalent volumes, if we regard the equivalent weights as numbers of grammes. The numbers 200 for sulphur, 406 for zinc, and 1350 for silver, then indicate that 406 grammes of zinc and 1350 of silver combine chemically with 200 grammes of sulphur. If we consider that all statements regarding specific weights, both of solid and fluid bodies, are calculated on the assumption that that of water is unity, and that 1 cubic centimeter of water weighs 1 gramme, then it follows that the specific weights of bodies express the numbers of

grammes that 1 c. c. of the body weighs. Thus, the numbers 1·99 and 6·95, the specific weights of sulphur and zinc, indicate that 1 c. c. of sulphur and 1 c. c. of zinc weigh respectively 1·99 and 6·95 grammes. Now since the equivalent volumes obtained on dividing the equivalent weight supposed to be expressed in grammes by the specific gravity (the weight of 1 c. c. expressed in grammes), it follows that the quotient, *the equivalent volume*, indicates the number of cubic centimeters occupied by that number of grammes of the body which expresses its equivalent weight. If we know that the equivalent weight and equivalent volume of sulphur are respectively 200 and 100, and that for zinc they are 406 and 58, then we can readily understand that 200 grammes of sulphur occupy a space of 100 c. c.; and 406 grammes of zinc a space of 58 c. c.

It is clear that the numbers for the equivalent volumes must differ according as, in reckoning the equivalents, we use those in which the equivalent of oxygen is assumed to be 100, or those in which the equivalent of hydrogen is regarded as 1, and therefore that of oxygen 8; but the relation of the equivalent volumes remains the same, exactly as the relation of the equivalent weight is unaffected, whether we take oxygen or hydrogen as our unit. Moreover it is obvious that those chemists who in individual cases make a difference between the equivalent weight and the atom weight, admitting a partition of the equivalent into two atoms, have also in these cases to make a difference between the equivalent volume and the atom volume. The equivalent and equivalent atom of iodine (I) is 1585, the specific weight is 4·93; hence we calculate the equivalent volume as $\frac{1585}{4\cdot93}$, or 320. The volume atom of iodine deduced from the density of its vapour (^{v}I), and the atom deduced from the specific heat of iodine (^{s}I), both weigh, however, only half as much as the equivalent, 792·5; the ^{v}atom volume or ^{s}atom volume amounts therefore to $\frac{792\cdot5}{4\cdot93}$, or 160, and is consequently only half as great as the equivalent atom volume.

The accuracy of the numbers expressing the equivalent volumes is naturally dependent on the accuracy with which the equivalent weights and specific weights are determined. When we consider that the former weights are only close approximations, and that regarding the latter we often meet

with very discordant statements, we cannot help acknowledging that these numbers are always to be regarded as only approximating in some measure to the truth, and thus it becomes obvious how it is that different chemists have assigned different numbers for one and the same body. The following table contains in the first column the names of the various elements (and of cyanogen) for which the equivalent volume is calculated from the equivalent weights arranged in the second column, and those specific weights which Kopp regards as most accurately determined, in the third column. The fourth column gives the result of this calculation, or the equivalent volume, in integral numbers.

Name.	Equivalent Weight.	Specific Weight.	Equivalent Volume.
Antimony	1613	6·72	240
Arsenic	937·5	5·86	160
Bismuth	2660	9·85	270
Bromine	1000	3·06	326
Cadmium	696·7	8·60	81
Chlorine	443·2	1·38	320
Chromium	328·5	5·10	64
Cobalt	368·5	8·39	44
Copper	396	9·00	44
Cyanogen	325	1·03	315
Gold	2458	19·10	128
Iodine	1585·5	4·93	320
Iridium	1232	21·60	57
Iron	350	7·70	45
Lead	1294	11·35	114
Mercury	1250	13·60	92
Molybdenum	596	8·68	68
Nickel	369·3	8·41	44
Osmium	1242·5	21·80	57
Palladium	665·5	11·70	57
Phosphorus	392	1·77	222
Platinum	1232	21·60	57
Potassium	489	0·84	583
Rhodium	652	11·40	57
Selenium	495	4·30	115
Silver	1350	10·40	130
Sodium	290	0·99	292
Sulphur	200	1·99	100
Tellurium	802	6·26	128
Tin	735·3	7·28	101
Titanium	301·5	5·33	56
Tungsten	1188	17·10	70
Zinc	406	6·95	58

From this table we at once observe that the equivalent volumes of the elements differ from one another to a remarkable degree; the equivalent volume of iron is 45, that of iodine 320, and that of potassium 583. On a closer examination we find that the equivalent volumes of several elements are either of the same magnitude, or stand in a simple relation to one another. We may select the following groups from the above table.

	Equiv. vol.		Equiv. vol.
Cobalt	45	Selenium	115
Copper	44	Sulphur	100
Iron	44		
Manganese	44	Gold	128
Nickel	44	Silver	130
Iridium	57		
Osmium	57	Bromine	326
Palladium	57	Chlorine	320
Platinum	57	Cyanogen	315
Titanium	56	Iodine	320
Zinc	58		
Chromium	64	Potassium	292
Molybdenum	68	Sodium	583
Tungsten	70		

It may be at once remarked that these groups in general embrace elements which yield isomorphous combinations.

Iron may, for instance, be replaced in a compound by an equivalent quantity (by weight) of manganese, without any change of form occurring to the compound, since the substituted quantity of manganese has an equal volume with the quantity of iron for which it was substituted, and therefore fills an equal space. But, as we shall presently show, the elements are not always held in combination with the same equivalent volume as they have in the isolated state; we therefore term the latter, the original equivalent volume.

The equivalent volume of a body must vary with the temperature, since bodies become expanded by warming, and be greater at a higher than at a lower temperature. In other words, since the specific weights of bodies diminish as those bodies are warmed, it follows that in calculating the equivalent volumes, the divisor becomes less in proportion as the temperature is increased: the quotient—the equivalent

volume—becomes, therefore, so much the larger. According to the atomic theory, the expansion of bodies on warming is dependent on an increase in the relative distances of the atoms. Atoms, together with the spaces intervening between them, or, as we generally express it, the surrounding spheres of heat, assume, therefore, a larger space in a higher than in a lower temperature; that is to say, the atom-volume is larger in the former than in the latter state.

The question now arises, at what temperature should the equivalent volumes of bodies be submitted to comparison with one another? That in this case corresponding temperatures are not equal temperatures is at once obvious, if we take into consideration the very different degrees of expansion which fluid and solid bodies undergo from an equal amount of heat. We shall subsequently find that for fluid bodies those are corresponding temperatures at which the tension of their vapours is equally strong, and that consequently at these temperatures the corresponding equivalent volumes must be determined, if we wish to institute a comparison between them. In the case of solid bodies, Kopp regards those temperatures as probably corresponding which lie equidistant from the fusion-points. For such bodies as have nearly similar fusion-points the same degrees of temperature denote also corresponding temperatures, and in such cases it must follow that the augmentation of the equivalent volumes is the same for similar elevations of temperature, and that a simple relation is established. Thus, according to Kopp, an equivalent volume of zinc increases in bulk on the temperature being raised from 32° to 212° F. almost exactly as much as an equivalent volume of tin, while an equivalent volume of bismuth increases to nearly double the extent; the same elevation of temperature increases to nearly the same degree an equivalent volume of platinum and an equivalent volume of palladium, while, if equivalent volumes of gold and copper are submitted to a similar elevation of temperature, the augmentation of the former is nearly twice as great as that of the latter. The equivalent volume of gold at 32° is fixed at 130, and that of copper at 44; by raising the temperature to 212° the former becomes increased to 130·46, and the latter to 44·23; so that while for the copper the augmenta-

tion is 0·23, the corresponding augmentation for the gold is $2 \times 0{\cdot}23$. It is scarcely necessary to remark that from this a partition of the equivalents of bismuth and gold into two atoms might be inferred. The equivalent volumes of the elements in the above table are calculated for the ordinary mean temperature, since the specific gravities used as divisors are the specific gravities at that temperature.

According to Schröder*, solid bodies are in corresponding states at such temperatures as are at corresponding distances from their fusion-heat, and in such conditions their equivalent volumes stand in the relations of whole numbers. At a temperature removed about as far from their fusion-points as the ordinary temperature from a red heat (400° to 1000° C.) the equivalent volumes of solid bodies are expressed by numbers which, taken together, are multiples of 4; these are termed by Schröder the theoretical equivalent volumes. They are collected in the following table:

Aluminum	60	Molybdenum	68
Arsenic	156	Nickel	44
Barium	144	Osmium	64
Bismuth	128	Oxygen	64
Bromine	368	Palladium	52
Cadmium	80	Phosphorus	220
Calcium	56	Platinum	52
Carbon	36	Potassium	240
Chlorine	240	Rhodium	56
Chromium	72	Selenium	112
Cobalt	44	Silver	128
Copper	44	Sodium	128
Gold	64	Strontium	104
Iodine	424	Sulphur	112
Iridium	52	Tellurium	128
Iron	44	Tin	100
Lead	112	Titanium	56
Manganese	44	Tungsten	68
Manganic acid	56	Zinc	56
Mercury	88		

It is evident that in order to determine the equivalent volumes of compounds we must proceed in exactly the same manner as in determining the equivalent volumes of the elements in their

* Schröder, die Molecularvolumina der chemischen Verbindungen. Mannheim, Fr. Bassermann, 1843. For a criticism of his Memoir, consult Kopp, Bemerkungen zur Volumtheorie. Braunschweig, 1844.

solid (or fluid) states; that is to say, we must divide the equivalent weight by the specific weight. The equivalent weight of oxide of copper, Cu O, for instance, is $396+100=496$; its specific weight is 6·4; the equivalent volume is therefore $\frac{496}{6\cdot4}=77\cdot5$. 496 grammes of oxide of copper (1 Eq.) consequently occupy a space of 77·5 cubic centimeters. The equivalent weight of sulphide of copper, Cu S, is $396+200=596$; its specific weight is 4·16; the equivalent volume is, therefore, $\frac{596}{4\cdot16}=144$. The equivalent weight of the disulphide of copper, Cu_2 S, is $2\times396+200=992$; the specific weight is 5·97; the equivalent volume is therefore $\frac{992}{5\cdot97}=166$, &c., &c.

The question now arises, in what relation do the equivalent volumes of compound substances stand to the equivalent volume of their constituents? Is the equivalent volume of the compound the sum of the equivalent volumes of its constituents, or does a condensation or an expansion accompany the chemical union? If, before discussing this question, we take a glance at the relation in which the volume of a gaseous compound stands to the volume of its gaseous constituents, we find that in many cases the volume of the compound is equal to the sum of the volumes of the constituents, but that in most cases a condensation, and, in a few instances, an expansion follows. If condensation or expansion follows, the relation of the volume of the compound to the volume of its constituents is invariably expressed by very simple numbers. For instance, 1 Eq.-vol. (2 vol.) of hydrogen gas and 1 Eq.-vol. (2 vol.) of chlorine gas give 1 Eq.-vol. (4 vol.) of hydrochloric-acid gas; the volume of the compound is the sum of the volumes of the constituents. 3 Eq.-vol. (6 vol.) of hydrogen gas and 1 Eq.-vol. (2 vol.) of nitrogen gas give 1 Eq.-vol. (4 vol.) of ammoniacal gas; hence it follows that with the chemical union there is a condensation in the relation of 8:4 or of 2:1; 1 Eq.-vol. (2 vol.) of hydrogen gas and 1 Eq.-vol. (1 vol.) of oxygen gas give 1 Eq.-vol. (2 vol.) of aqueous vapour; there being in this case a condensation in the relation of 3:2. 1 Eq.-vol. (2 vol.) of vapour of mercury and 1 Eq.-vol. ($\frac{1}{3}$ vol.) of vapour of sulphur form 1 Eq.-vol. (3 vol.) of vapour of sulphide of mercury, the chemical union being, in this instance, accompanied by an expansion in the relation of $2\frac{1}{3}:3$ or of 7 : 9.

If a condensation occurs in the union of gaseous elements we may, in various ways, conclude beforehand what is likely to occur. We may assume that the gases enter into the combination, which is then condensed, or we may suppose that one or other of the gaseous constituents, or all of them, become condensed previous to their combining, and that then, without further condensation, chemical union occurs. According to the former view, the compound suffers condensation, while, according to the latter, its constituents undergo this modification. For instance, in the union of 6 vol. of hydrogen gas and 2 vol. of nitrogen gas, we may either say that the 8 vol. of ammoniacal gas that are produced are condensed to 4 vol., or that the 6 vol. of hydrogen gas are condensed to 3 vol. (3 Eq.-vol.) and the 2 vol. of nitrogen gas to 1 vol. (1 Eq.-vol.) and that the union into the 4 vol. of ammoniacal gas now follows.

Let us now see in what relations the chemical union of solid bodies occurs; that is to say, in what relation the volume of the compound in the solid state stands to the volume of the constituents in the solid state. If there occur between the two, simple relations similar to those between the volumes of gaseous compounds and of their constituents, we are then in a condition to calculate from their solid compounds the equivalent volume of those elements which, in their isolated state, we cannot obtain in a solid form, as oxygen, hydrogen, &c., and knowing the equivalent volume of these elements, we likewise know their specific weight in the solid condition, since the latter is obtained on dividing the equivalent weight by the equivalent volume. In an analogous manner we may determine from their gaseous compounds the specific weight of the gases of such bodies as, isolated, cannot be obtained in the gaseous form, as, for instance, the specific weight of carbon vapour from the specific weight of carbonic acid gas.

We have already found that the equivalent volume of sulphide of copper, Cu S, is $\frac{596}{4 \cdot 16}$ or 144. The equivalent volumes of copper and sulphur are known, that of copper being 44, and that of sulphur 100; hence the equivalent volume of sulphide of copper is exactly equal to the sum of the equivalent volumes of its constituents. 44 cubic centimeters of copper (1 Eq.) and 100 c. c. of sulphur (1 Eq.) yield exactly 144 c. c. (1 Eq.) of sulphide of copper. The equivalent weight of sulphide of

silver, Ag S, is 1550, and the specific weight is 6·8; the equivalent volume is therefore $\frac{1550}{6\cdot8}$ or 228, a number which approaches quite as closely to the sum of the equivalent volumes of silver (130) and sulphur (100) as we have any right to expect; 130 cubic centimeters of silver and 100 c. c. of sulphur yield, therefore, 230 c. c. of sulphide of silver. The calculated specific weight of sulphide of silver is consequently $\frac{1550}{230}$ or 6·74, which does not differ from the observed specific weight by quite 1 per cent. (674 : 680 = 100 : 100·9.)

The equivalent volume of disulphide of copper, Cu_2 S, has been shown to be $\frac{992}{5\cdot97}$ or 166. The sum of 2 equivalent volumes of copper and 1 equivalent volume of sulphur is, however, 188, (namely, 44 + 44 + 100,) whence it follows that the equivalent volume of disulphide of copper does not directly correspond with the sum of the equivalent volumes of its constituents. The equivalent weight of bisulphide of iron, Fe S_2, is 750 (350 + 200 + 200,) and the specific weight is 5·08; the equivalent volume is therefore $\frac{750}{5\cdot08}$ or 147. On adding the equivalent volumes of the constituents, those namely of Fe and 2S, we obtain the number 245, and hence it follows, as in the disulphide of copper, that the equivalent volume of the bisulphide of iron is much smaller than the sum of the equivalent volumes of its constituents; a condensation must occur in the chemical union of the copper and sulphur into disulphide of copper, and likewise in that of the iron and sulphur into bisulphide of iron. The equivalent volume of potassium, if reckoned from its equivalent weight (489,) and its specific weight (0·84,) is 583. But the equivalent volume of the oxide of potassium, K O, if calculated from its equivalent weight (589,) and its specific weight (2·66) is 221, and therefore far smaller than that of potassium, one of its constituents; 583 cubic centimeters of potassium together with the oxygen required for oxidation have been condensed into 221 c. c. of potash.

The equivalent weight of the sulphide of arsenic, commonly known as realgar, As S_2, is 1337·5 (937·5 + 200 + 200,) and its specific weight is 3·56; the equivalent volume is, therefore, 375. The sum of the equivalent volume of the constituents of realgar amounts, however, to 360 (160 + 100 + 100,) and hence it follows that the equivalent volume of realgar is greater than the sum of

the equivalent volumes of its constituents; hence, in the chemical union of arsenic and sulphur into realgar, there must occur a negative condensation, or, in other words, an expansion.

As in the chemical union of elements in the states of gas or vapour, so also in the chemical union of elements in the solid condition we find that the volume of the resulting compound is either equal to, or smaller than, the volume of the constituents, in which latter case (one, by the way, of very frequent occurrence,) condensation must have taken place, or finally, that the volume of the compound is greater than the volume of the constituents, and that consequently an expansion takes place.

After Herapath, Boullay, and Karsten had sought in vain to find any regular law regarding the change in volume occurring in the chemical union of solid bodies, Kopp endeavoured to give formulæ for the calculation of the specific weights of compounds, from the specific weights and equivalent weights of their constituents, whereby he was led to conclude that condensation occurred in the resulting compound. (*Pogg. Annalen, Bd.* 47, *s.* 133—153.) By interesting comparisons of the specific weights of metals, combined with various proportions of oxygen and sulphur, with the equivalent weights, Ammermüller was led to the discovery of a principle which, according to Poggendorf, may be thus expressed: the specific weights of the compounds of a radical with an electronegative body are to one another, either directly as the equivalent weights (the atomic weight) of the compounds, or as multiples or sub-multiples of them. We may readily see that this proposition is identical with the following: the equivalent volumes of the compounds of a radical with an electronegative body are either equal to, or are multiples or sub-multiples of, one another. For instance, the specific weight of the dinoxide of copper is 5·749, and the specific weight of the oxide is 6·4; but 5·749 is to 6·4 as the equivalent weight of the dinoxide of copper is to twice the equivalent weight of the oxide of copper:—

Spec. weights. Equiv. weights.

$$Cu_2O : CuO = 5{\cdot}749 : 6{\cdot}4 = 892 : 496 \times 2$$

The equivalent volumes of the dinoxide and the oxide of copper are, by calculation, respectively $\frac{892}{5{\cdot}749}$ and $\frac{496}{6{\cdot}4}$, or 155 and 77·5; the former is therefore exactly double the latter. The

equivalent weights being in general determined with the greater accuracy, we may calculate the specific weight of one compound, on this principle, from that of another determined with sufficient accuracy. The following table gives the observed specific weights of different compounds, and the relation of the equivalent weights corresponding to them.

		Spec. weights.		Equiv. weights.	
SnO :	SnO_2 =	6·666 :	6·9 =	835·3 :	935·3
PbO :	PbO_2 =	8·01 :	9·19 =	1394·5 :	1494·5
Cu_2O :	CuO =	5·749 :	6·4 =	892 :	496 × 2
Hg_2O :	HgO =	10·69 :	11·29 =	2600 :	1350 × 2
SnS :	SnS_2 =	5·267 :	4·415 =	935·3 :	1135·3 × $\frac{2}{3}$
MnO :	MnO_2 =	4·726 :	3·760 =	444·7 :	544·7 × $\frac{2}{3}$
MnO :	Mn_2O_3 =	4·726 :	4·328 =	444·7 :	989·4 × $\frac{2}{5}$
Mn_2O_3 :	MnO_2 =	4·328 :	3·760 =	989·4 :	544·7 × $\frac{5}{3}$
AsS_2 :	AsS_3 =	3·544 :	8·459 =	1337·5 :	1537·5 × $\frac{4}{5}$
Hg_2Cl :	$HgCl$ =	7·14 :	5·42 =	2943·2 :	1693·2 × $\frac{1}{3}$

We must assume that there are very considerable errors in the determination of the specific weights, if we are to consider that this table serves for the confirmation of the above rule. If from the given relations of the equivalent weights we calculate the specific weight of one or the other compound, it is only in extremely few cases, as for instance in the dinoxide and oxide of copper, that we obtain a number in any degree approximating to the observed specific weight. The specific weights of the oxide and peroxide of lead ought, for instance, to be exactly in the relation of the equivalent weights of their compounds; and, therefore, as 1394·5 to 1494·5. Since the specific weight of the oxide can probably be determined with greater accuracy than that of the peroxide, we had better select the latter for calculation. We have then—

$$1394{\cdot}5 : 1494{\cdot}5 = 8{\cdot}01 : x, \text{ which therefore} = 8{\cdot}58.$$

In accordance with the rule in question, we calculate the specific weight of peroxide of lead at 8·58, while by direct experiment we find it to be 9·19. The specific weights of AsS_2 and AsS_3 should be to one another as the equivalent weight of AsS_2 to $\frac{4}{5}$ of the equivalent weight of AsS_3; that is to say, as $1337{\cdot}5 : 1537{\cdot}5 \times \frac{4}{5}$, or as 1337·5 : 1230. If again we calculate the specific weight of AsS_3 from that of AsS_2, we have $1337{\cdot}5 : 1230 = 3{\cdot}544 : x$, or $x = 3{\cdot}25$, while from direct observation we find that its specific weight is 3·459.

Schröder has laid down the following law regarding the relation of the equivalent volume of a compound to that of its constituents: the equivalent volume of every compound is the sum of the equivalent volumes of the constituents of the compound (elementary law); the equivalent volume of a constituent in a compound may differ from that which it possesses in an isolated condition, but in that case it always stands to the latter in a simple relation; that is to say, according to Schröder, in the relations of the numbers 1 : 2 : 3 : 4 : 5 : 6 (the law of condensation). According to this law, the positive or negative condensation (condensation or expansion) occurring in a chemical union was referred to the constituents; their equivalent volume is changed in simple proportions, and these, positively or negatively, condensed constituents unite to form the equivalent volume of the compound, (see p. 8). In the case of sulphur, for instance, Schröder assumed that it enters into combination with $\frac{4}{5}$, $\frac{3}{2}$, $\frac{1}{3}$, and $\frac{1}{2}$ the original equivalent volume. (*Pogg. Annalen, Bd.* 50, *s.* 553—604). We have already seen that the equivalent volume of disulphide of copper is expressed by the number 166, and that the sum of the equivalent volume of the constituents is 188 (88 + 100). According to Schröder's assumption, on the union of the copper and the sulphur the equivalent volume of the copper remains unchanged, namely, 88; while the equivalent volume of the sulphur, 100, is reduced to $\frac{4}{5}$, that is to say, to 80. 88 cubic centimeters of copper and 100 c. c. of sulphur condensed to 80 c. c. combine, therefore, to form 168 c. c. of disulphide of copper. The equivalent volume of bisulphide of iron, $Fe\,S_2$, commonly known as iron pyrites, is, as we have shewn by calculation, 147. The sum of the equivalent volumes of its constituents amounts to 245 (45 + 100 + 100). Schröder consequently assumed that the unchanged equivalent volume of iron combines with the equivalent volume of sulphur, condensed to one-half its bulk to form iron pyrites, (45 + 50 + 50 = 145).

Some time previously to Schröder's announcement of the law of the relation of the equivalents of compounds to the equivalent volume of their constituents, he made the discovery that if from the equivalent volume of compounds which contain a common constituent, we subtract the equivalent volume of the

other constituent an equal remainder is, in many cases, left for the aforesaid common constituent. The importance of this discovery is at once obvious; it indicates the mode by which we can find the equivalent volume of bodies in which it cannot be directly determined, since they are not to be obtained in the solid state; as, for instance, the equivalent volume of oxygen in the solid condition.

The following table exhibits this in the case of oxides; it contains in column A the equivalent, in column B the specific weight of the oxide, in column C the equivalent volume calculated from the above data, in column D the equivalent volume of the metal, and, finally, in column E the difference between the equivalent volume of the oxide and that of the metal (C − D).

TABLE I.

	A Equivalent.	B Spec. grav.	C Equiv. vol.	D Equiv. vol. of Metal.	E Difference. C−D.	
Cu O	496	6·4	77·5	44	33·5	
Zn O	506	5·43	92·6	59	33·6	
Cd O	796·7	6·95	114·8	81	33·8	
Pb O	1394·5	9·5	146·8	114	32·8	
Hg O	1350	11·0	123	92	31·0	
Fe_2O_3	1000	5·22	191·5	90	101·5	= 3×33·8
Co_2O_3	1037	5·6	185·4	88	97·4	= 3×32·5
$Sb O_3$	1913	5·56	344	240	104·0	= 3×34·6
$Ti O_2$	501·5	4·18	120	56	64·0	= 2×32

We thus find that for the equivalent volume of oxygen we obtain the same number, one nearly approaching to 32, if from the equivalent volume of these oxides we subtract that of the metal, and we may consequently well believe that the number 32 actually expresses the original equivalent volume of oxygen in the solid form. All oxides do not, however, give the same result, as we may see from the following table.

TABLE II.

	A Equivalent.	B Spec. grav.	C Equiv. vol.	D Equiv. vol. of Metal.	E Difference, C−D.	
$Sn O_2$	935·3	6·95	134·5	101	33·5	= 2×16·7
Cr_2O_3	957·0	5·21	183·7	128	55·7	= 3×18·3
Ag O	1450	7·25	200	130	70	
Cu_2O	892	5·75	155	88	65	
$Mo O_3$	896	3·4	264	69	195	= 3×65
$Wo O_3$	1488	6·12	243	69	174	= 3×58

In the two first-mentioned oxides the oxygen is contained with an equivalent volume of about 16, (and therefore $\frac{1}{2} \times 32$;) in the four last cases with an equivalent volume of 64, or 2×32.

If, in accordance with these tables, we express the equivalent volume of oxygen by the number 32, it affords a confirmation of the above-mentioned law of Schröder. In the formation of the oxides of copper, tin, and iron, in titanic acid, &c., the equivalents of the metal and the oxygen remain unchanged, the equivalent volume of the compound being the sum of the original equivalent volumes of the constituents. In the chemical union of tin with oxygen, forming oxide of tin, and in that of chromium with oxygen, forming oxide of chromium, a condensation of the equivalent volume of oxygen to one-half has taken place; while in the chemical union of silver and oxygen, forming oxide of silver, and in that of copper and oxygen, forming dinoxide of copper, the equivalent volume of the oxygen becomes enlarged to double its bulk.

The equivalent volume of potash has already been calculated as 222; the original equivalent volume of potassium is 583. If from the equivalent volume of potash we subtract that of oxygen, (namely, 32,) there remains 190 as the equivalent volume of the potassium in the potash; this number is pretty nearly $\frac{1}{3}$rd of 583, which expresses the original equivalent volume of potassium, for $3 \times 190 = 570$. Hence, in the formation of potash, a condensation of the equivalent volume of the potassium to $\frac{1}{3}$rd of its original volume has taken place. The equivalent volume of water is 112·5 $\left(\frac{112 \cdot 5}{1 \cdot 000}\right)$; if we subtract from this, 32, as the equivalent volume of oxygen, there remains the number 80·5 to represent the equivalent volume of hydrogen, if we assume that in the formation of water the hydrogen and oxygen unite in their original equivalent volumes.

It is easy to see that in accordance with Schröder's law the equivalent volumes of compounds may frequently be explained by the assumption of different degrees of condensation; this condensation occurring in either one or both constituents. The equivalent volume of titanic acid, $Ti\,O_2$, has been already found to be 120; on the supposition that the titanium and oxygen are contained in their original equivalent volume, the equivalent volume is by calculation $57 + 32 + 32 = 121$, which coincides

very well with observation. Schröder has, however, assumed that in titanic acid the equivalent volume of titanium is expanded to one and a half time its original bulk, while that of oxygen is condensed to one-half. We then obtain $\frac{3}{2} \times 57 + \frac{1}{2} \times 64$, or 117·5, as the equivalent volume of titanic acid; and similarly in many other cases.

More recently Schröder has modified his views; instead of considering that the condensation affects the individual constituents, he now believes that the condensation occurs in the compound that is formed. (See p. 9.) "When solid elements combine, the condensations which occur stand in the relation of whole numbers to the volume of the elements;" thus Schröder states the law which he regards as holding good*. We must not forget that, according to Schröder, the original equivalent volumes of the elements are multiples of 4, if the elements occur in corresponding conditions, (page 7). The condensations (whether positive or negative,) which occur in the union of the elements are expressed, according to Schröder, by the numbers 16 or 8, and by multiples of these numbers, and consequently of the number 4. According to Schröder's table given in page 7,

The equivalent volume of iron is	44
„ „ mercury	88
„ „ sulphur	100
„ „ chlorine	240

And therefore—

The volume of 2 eqs. of mercury	176
„ 1 eq. of chlorine	240
The equivalent volume of the constituents of Hg_2Cl	416
The condensation	0
The equivalent volume of Hg_2Cl (calomel)	416

Further—

The equivalent volume of mercury is	88
„ „ sulphur	100
The equivalent volume of HgS (cinnabar)	188
The condensation	8
The equivalent volume of cinnabar	180

* Die Molecularvolume der chemischen Verbindungen von H. Schröder. Mannheim, 1843.

Further—

The equivalent volume of the elements of iron pyrites, $Fe S_2$, (44 + 200)	244
The condensation	96
The equivalent volume of iron pyrites	148

In the memoir to which we have already alluded, Schröder has established, in accordance with this law, the equivalent volumes of various compounds—of oxides, sulphides, sulphates, carbonates, &c.,—and thence calculated their specific weights in order to show how far his theory is confirmed by experiment. For an element or constituent of compounds, of which the equivalent volume cannot be determined in its original state, from its not being obtainable in either a solid or isolable condition, he has calculated the equivalent volume according to this law from its compounds, in a manner which we shall proceed to investigate more closely.

With this view I insert an extract from the table that Schröder has calculated for the Oxides. I have not deemed it necessary to make any alteration in his equivalent weights, although some of them have been modified by more recent determinations; since, for our present object, they may as well remain as they are.

Oxides. "The empirical mean for the volume of oxygen deduced from 37 oxides is 64; I obtain it by increasing the observed volume of the oxide by the condensation that occurs, by subtracting from this value the volume of the metal, dividing the remainder by the number of atoms of oxygen, and taking the mean of all the values thus empirically determined. With the volume 64 ($= 8 \times 8$) for the atom of oxygen, I have, in the following table, explained the volume of the oxides."

TABLE III.

Substance.	Symbol.	Atomic Weight.	Sum of the Volumes of the Components.	Condensation.	Theoretical Volume.	Observed Volume.	Calculated Specific Gravity.	Observed Specific Gravity.
Suboxide of Copper	2Cu + O	892	88 + 64 = 152	0	152	149	5·87	5·99 Mohs, 5·75 Karsten, 5·72 Le Royer and Dumas.
Suboxide of Mercury	2Hg + O	2632	176 + 64 = 240	0	240	241	10·97	10·69 Herapath, 8·95 Karsten.
Lime	Ca + O	353	56 + 64 = 120	8	112	111	3·16	3·18 Boullay, 3·16 Karsten.
Oxide of Silver	Ag + O	1452	128 + 64 = 192	16	176	176	8·26	8·26 Karsten, 7·25 Boullay.
Oxide of Lead	Pb + O	1395	112 + 64 = 176	32	144	147	9·69	9·50 Boullay, 9·21 Karsten.
Oxide of Copper	Cu + O	496	44 + 64 = 108	32	76	77	6·53	6·43 Karsten, 6·13 Boullay.
Oxide of Mercury....	Hg + O	1366	88 + 64 = 152	32	120	121	11·39	11·29 Le Royer and Dumas, 11·19 Karsten.
Tungstic Acid	W + 3O	1483	68 + 192 = 260	48	212	208	6·99	7·14 Karsten, 6·12 Berzelius.
Soda	Na + O	391	128 + 64 = 192	56	136	139	2·88	2·81 Karsten.
Titanic Acid	Ti + 2O	504	56 + 128 = 184	64	120	118	4·20	4·15 to 4·20 Breithaupt, 4·25 Mohs.
Potash	K + O	590	240 + 64 = 304	80	224	222	2·64	2·66 Karsten.
Oxide of Iron	2Fe + 3O	978	88 + 192 = 280	96	184	186	5·32	5·25 Mohs, 5·23 Boullay.
Oxide of Chromium	2Cr + 3O	1004	144 + 192 = 336	144	192	193	5·23	5·21 Wöhler.

In the first place, the description of this table demands attention. "The empirical mean for the volume of oxygen, 64, was obtained by increasing the observed volume of the oxide by the condensation that occurs, by subtracting from this value the volume of the metal, &c." We naturally inquire by what means the condensations can be known, and how we are to learn what condensation must be applied in individual cases. We can, unfortunately, only reply that there is no certain controlling point for ascertaining the condensation. The condensations that occur are, according to Schröder, such as must be assumed in order that his own law of condensation may be best elucidated, and that the volume of oxygen assumed by him to be 64, may be explained in the clearest possible manner! At least, no other answer than this suggests itself to us. As we have already seen, very simple considerations render it so extremely probable that the equivalent volume of oxygen is 32, that we can hardly help looking upon Schröder's alteration of this number to 64 as unwarrantably arbitrary. Schröder was just as much in a position to draw up a table to represent the law of condensation if he had allowed the equivalent volume of oxygen to remain at 32. The condensation 32 for the oxides represented by the formula R O, the condensation 64 for $R O_2$, and 96 for $R_2 O_3$ and $R O_3$, would then naturally be omitted; that is to say, in all these oxides the equivalent volume would be exactly equal to the sum of the equivalent volumes of their constituents. When Schröder is not in a position to satisfy the law of condensation with the aid of the original (that is to say, the observed,) equivalent volume of a metal, he seems to consider himself entitled to alter the original equivalent volume into what he terms a theoretical equivalent volume. The oxide of chromium affords a proof of this statement. The oxide of chromium is $Cr_2 O_3$, its (old) equivalent weight is 1004, and its specific weight 5·21: hence the equivalent volume amounts, on calculation, to 193 $\left(\frac{1004}{5 \cdot 21}\right)$. The (old) equivalent weight of chromium is 352, and the specific weight 5·10; the equivalent volume is, consequently, 69. If, now, we assume, with Schröder, that the equivalent volume of oxygen is 64, then the sum of the equivalent volumes of the constituents of oxide of chromium is $330 = 69 + 69 + 64 + 64 + 64$. Accord-

ing to Schröder, the condensation amounts to 144 (9×16), and if we subtract this number from 330, there remains 186, as the theoretical equivalent volume of oxide of chromium. This number differs, however, too far from 192, (the number found in the direct manner,) and in order to obtain one more fitting to his views, he raises the equivalent volume of chromium, in what we must regard an arbitrary manner, from 69 to 72! The calculated equivalent volume is, then, 336 – 144, or 192. In this manner Schröder has obtained the theoretical equivalent volumes of the elements given in page 7, which, as we have already stated, are also multiples of 4. He regards the equivalent volume of chromium in the isolated state as 69, while in combination it is 72; he places the original equivalent volume of bismuth at 272, while in combination he regards it as 256! Kopp, in his *critique* on Schröder's work, has shown that we might just as properly consider the equivalent volumes of the elements to be multiples of 3 as multiples of 4. Although it may be deemed almost superfluous, we proceed to make an extract from Schröder's tables, calculated for sulphides and carbonates.

Sulphides (Sulphurets.) "If from the observed volume of any sulphide I subtract the volume of the metal diminished by the condensation that occurs, and divide the remainder by the number of atoms of sulphur contained in the combination, if I sum up the whole of the values thus obtained and divide by the number of observations, I obtain the whole number, 100, as the mean of the volume of an atom of sulphur. This value is especially deduced from 28 different bodies, and with it I have exhibited the volume of the metallic sulphides in the following table. It is to be observed that this value is an exact multiple of 4."

TABLE IV.

Substance.	Symbol.	Atomic Weight.	Sum of the Volumes of the Components.	Condensation.	Theoretical Volume.	Observed Volume.	Calculated Specific Gravity.	Observed Specific Gravity.
Sulphide of Cadmium	Cd S	898	80+100=180	−8	188	187	4·78	4·8 Brooke and Connel, natural; 4·61 Karsten, artificial.
Sulphide of Copper	Cu S	597	44+100=144	0	144	144	4·16	4·1 Karsten, artificial.
Zinc Blende	Zn S	604	56+100=156	8	148	148	4·08	4·078 Mohs, natural; 3·92 Karsten, artificial.
Cinnabar	Hg S	1467	88+100=188	8	180	181	8·14	8·124 Boullay, artificial; 8·098 Mohs, natural.
Silver Glance	Ag S	1553	128+100=228	16	212	216	7·32	7·20 Mohs, natural; 6·85 Karsten, artificial.
Copper Glance	Cu_2 S	993	88+100=188	16	172	166	5·78	5·98 Karsten, artificial; 5·75 Mohs, natural.
Galena	Pb S	1496	112+100=212	16	196	193	7·63	7·76 Beudant, natural; 7·51 Karsten, artificial.
Mosaic Gold	Sn_2 S	1138	100+200=300	48	252	247	4·52	4·6 Karsten, 4·42 Boullay.
Antimony Ore	Sb S_3	2217	240+300=540	64	476	467	4·66	4·75 Karsten, artificial; 4·62 Mohs, natural.
Iron Pyrites	Fe S_2	742	44+200=244	96	148	146	5·02	5·08 Breithaupt; 5·03 Mohs.

As in the case of oxygen so also for sulphur, we find Schröder calculating the equivalent volume from the sulphides (as in the other case he had done from the oxides), in accordance with the condensation that occurs, or, in other words, with the condensation that best suits his views, and it must be regarded as a complete chance that the equivalent volume (100) thus calculated is equal to the original equivalent volume. With an equal amount of probability we might deduce the number 108 from the sulphides as the equivalent volume of sulphur; all that would be required being merely an altered condensation. For sulphide of cadmium, Cd S, we should have $80+108$, or 188, as the equivalent volume, and the condensation would therefore be 0; for sulphide of copper, Cu S, we should have $44+108$, or 152, and therefore the condensation 8; for sulphide of zinc (blende), and sulphide of mercury (cinnabar), the condensation would be 16. For disulphide of copper it is $88+108$, or 196; or if we assume the condensation to be 32, we obtain 164 as the equivalent volume, which coincides far better with the number actually observed than the number 172 calculated by Schröder. He has likewise made changes in the original equivalent volume which we can only regard as arbitrary, in order to obtain multiples of 4. Thus the original equivalent volume of mercury is altered from 92 to 88, and that of silver from 130 to 128.

Carbonates. "When from the observed volume of any carbonate I subtract the volume of the metal and augment the remainder by the condensation that occurs (which is always a multiple of 16,) I obtain as a mean the number 172. This is again an exact multiple of 4. I have consequently assumed 172 as the volume with which, in case there is no condensation, one atom of carbon and three of oxygen combine in the carbonates. The volume of carbon is 36, and that of three atoms of oxygen is 3×64, or 192; hence the original volume of CO_3 is 228; the smallest condensation of CO_2 in the carbonates is therefore $228-172$, or 56, which $=7\times8$. If we start from the original volume of carbon and oxygen, then all the condensations occurring in the carbonates are multiples of 8, not of 16, but they progress from 16 to 16."

For the sake of convenience I will present this table as Kopp gives it in his remarks on the volume theory.

TABLE V.

Formula.	Sum of the Volumes of the Components.	Condensation.	Theoretical Volume.	Observed Volume.
$CaCO_3$ .... (Calc spar.)	56 + 172 = 228	0	228	231
$CaCO_3$ .... (Arragonite.)	56 + 172 = 228	16	212	209
$AgCO_3$	128 + 172 = 300	16	284	284
$CdCO_3$	80 + 172 = 252	16	236	239
$FeCO_3$	44 + 172 = 216	32	184	185
$BaCO_3$	144 + 172 = 316	32	284	284
KCO_3	240 + 172 = 412	32	380	383
$ZnCO_3$	56 + 172 = 228	48	180	176

And here we cannot refrain from observing that the assumption that 172 expresses the equivalent volume of CO_3 is altogether arbitrary, and that we may with equal propriety substitute another number in its place; for equally correct results are then obtained, if we only assume that a different degree of condensation ensues. If for instance, in place of 172 we substitute 188, or 172+16, as the equivalent volume of CO_3, the table assumes the following appearance.

TABLE VI.

Formula.	Sum of the Volumes of the Components.	Condensation.	Theoretical Volume.	Observed Volume.
$CaCO_3$ .... (Calc spar.)	56 + 188 = 244	16	228	231
$CaCO_3$ .... (Arragonite.)	56 + 188 = 244	32	212	209
$AgCO_3$	128 + 188 = 316	32	284	284
$CdCO_3$	80 + 188 = 268	32	236	239
$FeCO_3$	44 + 188 = 232	48	184	185
$BaCO_3$	144 + 188 = 332	48	284	284
KCO_3	240 + 188 = 428	48	380	383
$ZnCO_3$	56 + 188 = 244	64	180	176

Nor should we be less correct in assuming 172 − 16, or 156, as the equivalent volume of CO_3; the table becoming then modified in the following manner.

TABLE VII.

Formula.	Sum of the Volumes of the Components.	Condensation.	Theoretical Volume.	Observed Volume.
$Ca\,C\,O_3$ .... (Calc spar.)	56 + 156 = 212	−16	228	231
$Ca\,C\,O_3$ .... (Arragonite.)	56 + 156 = 212	0	212	209
$Ag\,C\,O_3$	128 + 156 = 284	0	284	284
$Cd\,C\,O_3$	80 + 156 = 236	0	236	239
$Fe\,C\,O_3$	44 + 156 = 200	16	184	185
$Ba\,C\,O_3$	144 + 156 = 300	16	284	284
$K\,C\,O_3$	240 + 156 = 396	16	380	383
$Zn\,C\,O_3$	56 + 156 = 212	32	180	176

It might be maintained that there is greater probability in the correctness of the number 156 for the equivalent volume of $C\,O_3$ than in Schröder's assumed number 172.

It is obvious, then, that Schröder's law of condensation is not founded on any safe basis; in leaving the subject I will make one further remark called forth by the last table. Carbonate of lime as calc spar, and carbonate of lime as arragonite, have a different equivalent volume in consequence of their having a different specific weight; thus, in general, *dimorphous bodies are distinguished from one another by a different equivalent volume.*

Carbon as diamond has a specific weight of 3·5, and therefore an equivalent volume of $\frac{75}{3\cdot5}$, or 21; as graphite it has a specific weight of about 2, and therefore an equivalent volume of $\frac{75}{2}$, or 37. According to Schröder a condensation amounting to 16 would have to be assumed in the diamond. Kopp is of opinion that the earlier view of Schröder is the correct one, namely, that the condensation occurring in chemical union is not to be referred to the compound but to the constituents, but he considers that this degree of condensation does not follow any simple relations. In an admirable memoir in the *Journal f. prakt. Chemie*, (1845, Bd. xxxiv., s. 1,) Kopp has explained the views which led him to the consideration of this subject, and I cannot do better than give the following epitome of his view, as drawn from that essay.

In the first place, Schröder's discovery that an equal residue is left on subtracting the equivalent volume of a common constituent from the equivalent volumes of analogous compounds, gave, as it were, a starting-point for rational considerations respecting the formation of the equivalent volumes of compounds; to considerations indeed which, according to Kopp, are probably still far from correctly exhibiting the natural laws which govern the combining relations of bodies in regard to bulk, but which, however, give extremely simple expressions for the equivalent volume and for the weight of many compounds.

For an individual and isolated compound no view can be shown to be even probably true of the equivalent volumes of the constituents contained in it, since from a single observation concerning the equivalent volume of the compound nothing can be concluded respecting several unknown magnitudes, (namely, the volumes which two or more constituents have when in combination). But for analogous compounds, views, possessing more or less probability, may be advanced regarding the equivalent volumes which we have to assign to the individual constituents.

If we revert to our former supposition that the equivalent weights indicate so many grammes, then 1 eq. of lead (Pb) weighs 1294 grammes, and the space which it occupies amounts to 114 c. c., (or the equivalent volume of Pb is 114). If we transform this quantity of lead into nitrate of lead we unite the elements of NO_6 to the lead. The lead increases in weight by 775 grammes, and in volume by 356 c. c., since the volume of the nitrate of lead that is formed is 476 c. c.; the equivalent is 2069, and the specific weight 44, and $\frac{2064}{4 \cdot 4}$ is equal to 476. An equivalent of silver weighs 1352 grammes, and its volume is 130 c. c. On converting it into a nitrate the elements of NO_6, amounting in weight to 775, unite with it, and its volume increases to 356 c. c.; the volume of nitrate of silver is 486, or 130+356.

These phenomena are very simply embraced in the assumption that the equivalent volume of lead or of silver remains unchanged in the nitrate just as it exists in those metals in the uncombined state; the equivalent volume of the elements

$N O_6$, which convert a metal into a nitrate, being taken with it, which in the nitrates is 356.

From such considerations Kopp* has sought to determine for various other groups of elements whose addition converts a metal into a salt, the equivalent volumes which must be assigned to them in such compounds. An equivalent of lead (1294 grammes) occupies 114 c. c.; in the process of conversion into oxide of lead, in which 100 grammes of oxygen are taken up, the volume becomes enlarged by 32 c. c. An exactly equal augmentation of volume takes place if we oxidize an equivalent of copper (396 grammes, or 4 c. c.), or of mercury (1250 grammes, or 92 c. c.), or of zinc (406 grammes, or 58 c. c.), 100 grammes of oxygen being in every case taken up. An equivalent of titanium (302 grammes) occupies 56 c. c.; if it is converted into titanic acid, in which case it takes up 200 grammes of oxygen, its volume becomes enlarged by 64, that is to say, by 2×32 c. c. Two equivalent volumes of iron (700 grammes) occupy 90 c. c.; if we convert them into peroxide of iron, in which case they take up 300 grammes of oxygen, their volume becomes increased by about 3×32 c. c.

All the facts are therefore simply explained on the assumption that the equivalent volume of the metals in question is the same in these oxides as that which the metals have in an isolated state; the volume of one eq. of oxygen, moreover, being 32, (100 grammes of oxygen in these oxides filling the space of 32 c. c.)

In this manner Kopp has sought to determine the equivalent volume of oxygen and similar bodies in their combinations. If, as we have already presumed, the equivalent volume of the metals remain unchanged in these combinations, this assumption leads to satisfactory results for the equivalent volumes of other constituents also, in the compounds of antimony, lead, cadmium, chromium, iron, cobalt, copper, manganese, molybdenum, nickel, mercury, silver, titanium, bismuth, tungsten, tin, and zinc; in short, in the compounds of the dense metals. These all, with the exception of arsenic, appear to be

* Kopp, über das specifische Gewicht der chemischen Verbindungen. Frankfurt A. M., 1841.

contained in their compounds with their original equivalent volume.

But the case is otherwise with the light metals; those, namely, of the alkalies and earths. These are contained in their combinations with an equivalent volume different from that which they possess in an isolated state. An equivalent of potassium, for instance, (489 grammes) fills a space of 583 c. c. If we convert this into sulphate of potash we obtain 1089 grammes of that salt, occupying a space of 420 c. c. It is impossible that the potassium contained therein can fill a space of 583 c. c. We must, therefore, assume that potassium (and similarly the other light metals, whose equivalent volume we often do not know in the isolated state,) has, when in its combinations, an equivalent volume different from that which it possesses in the isolated state. When we calculate what the equivalent volumes of such metals are in combination, we arrive at the result that each of the light metals possesses the same equivalent volume in all its analogous combinations; that is to say, in all its salts. Kopp proceeds in the following manner:—

Since the equivalent volume of the nitrates of lead and silver is larger by 356 than that of lead or silver, we have already concluded that the equivalent volume of $N O_6$ is 356 in these salts. The equivalent volume of nitrate of potash (K with the elements $N O_6$) is 590. If we assume that $N O_6$ is contained therein with the equivalent 356, it follows that the potassium contained in this salt must be $590 - 356$, or 234.

The equivalent volume of sulphate of lead (Pb with the elements of $S O_4$) is greater by 186 than that of lead, whence we conclude that the elements of $S O_4$ are contained in sulphate of lead with the equivalent volume 186. The same occurs in sulphate of potash, whose equivalent volume is 420, and the equivalent volume of the potassium contained therein must be $420 - 186$, or 234. This is the same number as that previously found, and Kopp consequently assumes that 234 represents the equivalent volume of potassium in its salts. By considerations of a similar nature, Kopp has obtained the following values for the equivalent volumes of the light metals in their salts, and also for ammonium:—

	Equiv. volume.
Ammonium	218
Barium	143
Calcium	60
Magnesium	40
Potassium	234
Sodium	130
Strontium....	108

If we assume that the equivalent volume of $C O_3$ (the elements by whose union with metals the carbonates are formed,) is 159; that the equivalent volume of the heavy metals is of the magnitude we have given in page 4; and that, that of the light metals is correctly given in the above table; then the equivalent volumes of carbonates of Pb, Cd, Fe, Mn, Ag, Zn, Ba, Ca, K, Mg, Na, and Sr, agree very well with the results of observation. For instance, the equivalent volume of lead is 114, that of carbonate of lead ($Pb + C O_3$) is calculated at $114 + 151$, or 265; since the equivalent of the salt is 1669, the specific weight is $\frac{1669}{265}$ or 6·3. The equivalent volume of strontium in its salts is 108; that of the carbonate of strontium is, therefore, calculated at $108 + 151$, or 259, and since the equivalent weight of the carbonate is 921, the specific weight is $\frac{921}{259}$ or 3·55.

With the same assumptions regarding the equivalent volumes of the metals, and presupposing that the equivalent volume of $N O_6$ (the elements with which the metals form nitrates) is 356, we may calculate the equivalent volume and the specific weights of the nitrates of Pb, Ag, Am (ammonium), Ba, K, Na, Sr, and the result will be found to accord entirely with observation.

The supposition that in the sulphates the elements of $S O_4$ have an equivalent volume of 236, explains the equivalent volume and the specific weight of the sulphates of Cu, Ag, Zn, Ca, Mg, and Na. But certain other sulphates render another supposition requisite; namely, that the elements of $S O_4$ are contained in them with an equivalent volume of 186; this is necessary for the sulphates of Pb, Ba, K, and Sr.

In discussing other classes of compounds in the same manner the volume of an element proves to be equally variable in its compounds. Such an assumption, however, does not appear to be opposed to nature, since the fact that dimorphous bodies have different equivalent volumes leads directly to it. As far as

concerns the sulphates, it appears not impossible that there is a change from a modification where SO_4 has the equivalent volume 186, into another modification in which SO_4 has the equivalent volume 236. The emission of light which occurs on the crystallization in water of sulphate of potash which has been fused with sulphate of soda, seems to indicate that the former by its fusion with $NaSO_4$ undergoes a modification in which SO_4 acquires the equivalent volume 236, and that on its crystallization it passes into a denser state, in which the equivalent volume of SO_4 is 186.

The assumption that the equivalent volume of CrO_4 is 288, and that of WO_4 244, accurately yields the equivalent volumes and specific weights of the chromates of Pb and K, and of the tungstates of Pb and Cu. The metallic chlorides are the only haloid salts whose equivalent volumes have been ascertained with any degree of certainty. Kopp assumes* that Cl has the equivalent volume 196 in its combinations with Pb, Ag, Ba, Na, and the equivalent volume 245 in its combinations with Am, Ca, K, Cu_2, Hg, Hg_2, Sr, and these views agree well with the observations made on the density of these salts.

If we assume the equivalent volume of the dense metals to remain the same in their oxides as already stated, (see p. 4,) but that the equivalent volume of oxygen becomes 32, we shall find that the equivalent volume, and consequently, also, the specific weight of the oxides, PbO, CdO, CuO, HgO, ZnO, SnO, TiO_2, SbO_3, Fe_2O_3, Co_2O_3, $FeTiO_3$†, agree closely with the results of observations. Thus, for instance, we have as the equivalent volume for SbO_3, $240+3\times32=336$, and since the equivalent weight of $SbO_3=1913$, the specific weight is $\frac{1913}{336}$ or 5·69. The equivalent volume of oxygen cannot, however, be assumed to be 32 in certain other oxides. If, for instance, we oxidize 1 equiv. tin (735 gram.), occupying 101 c. c., to form oxide of tin, the 2 equiv. of oxygen that are added occasion an augmentation of volume of 32 c. c.; 1 equiv. oxygen (100 gram.) occupying, therefore, a space of 16 c. c. in this oxide. We may assume that the equivalent volume of oxygen is 16 in SnO_2, as it is in Cr_2O_3. Finally, we may consider

* In page 571 of the work referred to.

† Titanate of Iron: Ilmenite.

the equivalent volume of oxygen to be 64 for the oxides Cu_2O, Ag O, Hg_2O, $Mo O_3$. (See p. 14.)

Such is the manner in which Kopp proceeds in considering the relations of volume of solid chemical combinations, and which he confesses to be merely relatively probable, and not entitled to more credit in their further developement, than the apparent correctness of certain unavoidable deductions confer upon them. Such, for instance, is the confirmation they give to the Radical theory of salts, highly probable on other grounds.

We shall now turn to the equivalent volume of liquids. Observations upon liquids have an especial interest, from showing more clearly than in solid bodies, how the change of equivalent volumes by temperature is to be considered.

Kopp found, in 1841, (*Annalen der Chemie und Pharm.* 1842, Bd. iii. s. 99), that analogous fluid compounds exhibit like differences in their equivalent volume; that, for instance, the equivalent volume of a hydrated acid is smaller by 534 than that of the corresponding ethyl combination, and smaller by 300 than the corresponding methyl combination, and consequently that the equivalent volume of every ethyl combination is greater by 234 than the corresponding combination of methyl, for instance,—

	Spec. Grav.	Equiv.	Equiv. vol.	Difference.
Hydrated acetic acid	1·063	753·3	708·7	
$\overline{A}$ + H O	Mollerat.			531·8
Acetate of the oxide of ethyl	0·89 at 15° C.	1106·7	1243·5	
$\overline{A}$ + E O	Liebig.			
Hydrated formic acid	1·2353 at 12°	576·7	466·8	
$\overline{F}$ + H O	Liebig.			532·9
Formiate of the oxide of ethyl	0·912	930·0	1019·7	
$\overline{F}$ + E O	Liebig.			

Further,—

Hydrated acetic acid	1·063	753·3	708·7	
$\overline{A}$ + H O	Mollerat.			303·3
Acetate of the oxide of methyl	0·919 at 22°	930·0	1012·0	
$\overline{A}$ + Me O	Dumas and Peligot.			

Finally,—

Alcohol	0·792 at 18° C.	578·3	729·9	
E O + H O	Gay Lussac.			226·6
Wood-spirit	0·798 at 20°	401·6	503·3	
Me O + H O	Dumas and Peligot.			

	Spec. Grav.	Equiv	Equiv. vol.	Difference.
Acetate of the oxide of ethyl	0·98 at 15°	1106·7	1243·5	231·5
$\bar{A} + EO$	Liebig.			
Acetate of the oxide of methyl	0·919 at 22°	930·0	1012.0	
$\bar{A} + MeO$	Dumas and Peligot.			
Hydrated acetic acid	1·063	753·3	708·7	244·9
$E + (O_3 + HO) - H_2$	Mollerat.			
Hydrated formic acid	1·2353 at 12°	576·7	466·8	
$Me + (O_3 + HO) - H_2$	Liebig.			

It is easy to see that by this law, if we know the specific weight of the hydrated acid, we may calculate the specific weight of the combinations of the acid with the oxide of ethyl and methyl, and further, that from the specific weight of an oxide of ethyl compound, we may calculate the specific weight of the corresponding compound of the oxide of methyl. If, for instance, to the equivalent volume of a hydrated acid we add the number 534, and divide the equivalent weight of the corresponding ethyl compound by this sum, we obtain the calculated specific weight, thus, the equivalent volume of hydrated acetic acid is 708·7, and adding to this 534, we have 1242·7, with which we must divide the equivalent weight of the acetate of oxide of ethyl; $\frac{1106·7}{1242·7}$ gives 0·8906 as the calculated specific weight, which perfectly coincides with 0·89 the number experimentally determined. Or: the equivalent volume of the acetate of oxide of ethyl is 1243·5, from which, if we subtract 234 there remains 1009·5; with which we must divide the equivalent of the acetate of oxide of methyl, 930; the quotient representing the specific weight is 0·921, while the number actually observed is 0·919. Kopp even regards the difference as only approximative, since in their estimation, the influence exercised by the temperature on the specific weight and on the equivalent volume has not been accurately considered.

At a subsequent period, Kopp examined more accurately the manner in which the temperature is to be considered in the determination of the equivalent volume, and found, as also did Schröder, *that the equivalent volumes of liquids should be compared at those temperatures at which their vapours possess equal tension.* Such temperatures are named corresponding temperatures. The boiling-points of fluids under the same atmospheric pressure are, for instance, corresponding temperatures in relation to their

equivalent volumes, but in relation to the elasticity of their vapours, the corresponding temperatures are not so high. The following considerations will render this statement more obvious:—

The equivalent of ether is 462·5;	its specific weight	0·724	at	12°·5 C.
„ „ water is 112·5;	„ „	1·000	at	„
„ „ alcohol is 575;	„ „	0·7923	at	17°·8

Hence we calculate:—

The volume of 1 eq. of ether	at 12°·5 =	638	750·5
„ water	„	112·5	
„ „ alcohol	at 17°·8 =		726·0

If ether and water form alcohol without the occurrence of condensation, both in the state of vapour and that of a liquid, then the equivalent volume of the alcohol must be equal to the sum of the equivalent volumes of the ether and water. The equivalent volume of alcohol at 17°·8 C. is as we have seen 726; but the sum of the equivalent volumes of ether and water at 55°·5 is 750. The case would be very different if we considered the equivalent volumes of these three bodies at corresponding temperatures, namely at the boiling-point.

According to Gay-Lussac when the barometer stands at [0m 76] 29·8 inches,—

The boiling-point of ether is	....	35°·7 C.	....	96·3° F.
„ „ water	....	100°	....	212° F.
„ „ alcohol	....	78°·4	....	173° F.

Gay-Lussac has also examined the change of volume which these substances undergo when exposed to heat: from these investigations it follows that—

The specific weight of ether	at the boiling-point	(35°·7)	is	0·69739
„ „ water	„ „	(100°)	„	0·96064
„ „ alcohol	„ „	(78°·4)	„	0·73869

If now we calculate the equivalent volume of these bodies at the boiling-point, we obtain:

The equivalent volume of ether at the boiling-point	$= \frac{462{\cdot}5}{0{\cdot}6974} =$	663·3	780·4
„ „ water „ „	$= \frac{112{\cdot}5}{0{\cdot}96064} =$	117·1	
„ „ alcohol „ „	$= \frac{575}{0{\cdot}739} =$		780·0

And we know that at the boiling-point the equivalent volume of alcohol is in point of fact exactly the same as the sum of the equivalent volumes of its constituents, ether and water.

But this also holds good for other corresponding temperatures. Half the tension for which the volumes are calculated, namely the tension corresponding to a column of mercury of 0^m 38, causes ether to assume the state of vapour at 20°·7, water at 81°·7, and alcohol at 61°·4; these, therefore, are corresponding temperatures for ether, water, and alcohol; they lie 15°, 18°·3, and 17° respectively below the boiling-points of these fluids, and we assume generally that *those are corresponding temperatures which lie equally distant from the boiling-point*, if they are not determined by direct experiment or by calculation. At a temperature of 20°·7, the equivalent volume of ether is 647·7; at 81°·7 that of water is 115·7; hence the sum is 763·4; but the equivalent volume of alcohol at 61°·4 is 764·7, and therefore equal to this sum.

According to Schröder the equivalent volumes of fluids stand to one another in the relation of whole numbers. Thus, according to him:

The equivalent volume of ether at the boiling-point being					663·3	which = 17 × 39·03
„	„	water	„	„	117·1	= 3 × 39·03
„	„	alcohol	„	„	780·0	= 20 × 39·03

the numbers 17, 3, and 20 express the relative relation of the equivalent volumes of ether, water, and alcohol, and thus the equivalent volumes of all fluids at the boiling-point must be simple multiples of the number 39·03. Kopp has examined the value of this theory in the *Annalen der Chemie und Pharmacie*, 1844, bd. 50, s. 115, to which I must refer my readers.

We have already seen that the ethyl compounds have usually an equivalent volume greater by 234 than the corresponding methyl compound. Now since ethyl = C_4H_5, and methyl = C_2H_3, ethyl is distinguished from methyl by an excess of C_2H_2, and to this association of elements we must ascribe the excess of the equivalent volume (234) occurring in its compounds. But in the different ethyl and methyl compounds which consist only of carbon, hydrogen, and oxygen, *all* the equivalents (atoms) C, O, and H, must have constant

equivalent volumes (atom-volumes), otherwise the constant difference of composition, $C_2 H_2$, would not give rise to a constant equivalent volume. Now in order to be able to determine the equivalent volumes of C, H, and O, for all corresponding temperatures, we must have three fluids consisting of these elements, for which the equivalent volume at any distance from the boiling-point is accurately known. Water, ether, and alcohol are fluids of this nature. Kopp has, however, explained why it is that from these three fluids we cannot deduce the three unknown magnitudes. (*Annal. d. Chem. und Pharm.*, 1844, bd. 50, s. 78.) The consideration of these points leads, however, to the very important result that H+O (water) and 4C+5H+O (ether), taken together at corresponding temperatures occupy the same space as 4C+6H+2O (alcohol), although of the two first fluids *one* equivalent in a state of vapour occupies *two* volumes; while *one* equivalent of alcohol in a state of vapour occupies *four* volumes. Hence, for C, H, and O, at equally great distances from the boiling-point, we have the same equivalent volumes in a liquid which is condensed from two volumes of vapour, as in another which is condensed from four volumes. At corresponding temperatures C, H, and O have the same equivalent volumes in all fluids, even if when converted into vapour they exhibit different degrees of condensation (Op. cit. s. 79). An assumption led Kopp to a mode by which he might, at least approximately, determine the equivalent volumes of C, H, and O, when in combination; namely, the hypothesis *that the equivalent volume of a compound does not undergo any considerable change, probably none at all, if one equivalent of oxygen be substituted in it for one equivalent* (2 *volume-atoms*) *of hydrogen*, and the measurement of the equivalent volumes of the compounds be always determined at an equally great distance from the boiling-point, (or more correctly, at those temperatures at which there is an equal tension of the vapour).

Alcohol ($C_4 H_6 O_2$) and acetic hydrate ($C_4 H_4 O_4$) differ in their formulæ by the latter containing 2 eq. of oxygen more, and 2 eq. of hydrogen less than the former; in other words, 2 eq. of hydrogen of the former are replaced in the

latter by 2 eq. of oxygen. Now $C_4 H_4 O_4$, representing 750 grammes of acetic hydrate, the specific gravity at 16° being according to Mollerat 1063, occupies a space of 705 c. c., at a temperature which is distant 104° from the boiling-point of acetic acid, (120° C., Liebig); but $C_4 H_6 O_2$, representing 575 grammes of alcohol, occupies a space of 695·4 c. c., at a temperature which is also 104° from its boiling-point (78°·4 according to Gay-Lussac), that is to say, at − 25°·6, and hence it follows that acetic hydrate and alcohol at corresponding temperatures have a similar equivalent volume, since the equivalent volume of 2H is equal to that of 2O.

If we represent the equivalent volume of oxygen by (O), and that of hydrogen by (H), then from what we have already stated (O)=(H). But from observations it follows that the equivalent volume of water (H O) at its boiling-point is 117, and hence it follows that (H) =58·5, and (O) =58·5, in liquid combinations at their boiling-points.

The equivalent volume of carbon (C) can only be found in the following manner. In accordance with observations, the equivalent volume of ether ($C_4 H_5 O$) at its boiling-point is 663, which is the sum of 4(C)+5(H)+(O). But from what has been already stated, 5(H)+(O)=5×58·5 +58·5=351, and this subtracted from 663 gives 312 as the value of 4(C). Hence (C)=78. This is the equivalent volume of carbon in liquid combinations at their boiling-points. We arrive at the same number if, from the equivalent volume of alcohol at its boiling-point, 780, we subtract 6(H)+2(O), or 468, and divide the remainder by 4.

For the boiling-point we have, therefore, the following equivalent volumes,

(C)=78, (H)=58·5, and (O)=58·5.

It is of assistance in calculations to regard the equivalent volumes of carbon, hydrogen, and oxygen as products having a common factor. The numbers we have just found may be very simply expressed in the following manner.

(C)=78=8×9·75; (H) and (O)=58·5=6×9·75.

And hence, at the boiling-point the equivalent volumes of carbon, hydrogen, and oxygen stand in the simple relations of 8 : 6 : 6.

We must now consider the question, does this relation hold good for corresponding temperatures below the boiling-points, and does the same or a different relation hold good for all corresponding temperatures under the boiling-point? or (in other words) have C, H, and O, in liquid compounds, a similar or a different dilatability? Kopp confesses his inability to answer this question.

The assumption that the given relation holds good at all corresponding temperatures is supported by no analogy; in the metals in their isolated state this regularity is not observed, if, in their case, we regard those as corresponding temperatures which are equally distant from the fusion-point. In order that this regularity might occur, it would be requisite that every simple metal, with nearly the same fusion-point, should exhibit a similar capacity of expansion between 0° and 100°, which, however, is not the case.

This assumption, however, which Kopp in the most decided manner explains as perfectly arbitrary, permits the experimental approximate determination of the equivalent volumes of C, H, and O, and leads to a formula by which the density of many liquid compounds may be expressed with remarkable accuracy.

We may by this assumption regard the diminution of the equivalent volumes of C, H, and O as a diminution of the common factor, 9·75. The amount by which this factor diminishes for a temperature distant by a definite number of degrees, D°, from the boiling-point, has been attempted to be determined by Kopp, in the following manner. According to Gay-Lussac the equivalent volume of ether, which boils at 35°·7, is at $-19°{\cdot}3 = 612{\cdot}9$; this temperature is 55° from the boiling-point; hence, in this case, $D = 55$. The equivalent volume of ether at the boiling-point calculated from the equivalent volume of C, H, and O: $C_4 H_5 O$: is $4 \times 78 + 5 \times 58{\cdot}5 + 58 = 663$. The equivalent volumes of C, H, and O must, therefore, at the boiling-point and at $-19°{\cdot}3$, stand to one another as 663 : 612·9. Hence we have,

663 : 612·9 : : 78·0 : x; $x = 72{\cdot}1$ (C)
663 : 612·9 : : 58·5 : x; $x = 54{\cdot}08$ (H)
663 : 612·9 : : 58·5 : x; $x = 54{\cdot}08$ (O)

Hence, at $-19°{\cdot}3$, C has an equivalent volume of 72·1, while that of H and O is 54·08. These numbers may, however, be expressed as $8 \times 9{\cdot}01$ and $6 \times 9{\cdot}01$; and hence for a depression of temperature of 55° (D = 55).

The common factor undergoes a diminution from 9·75 to 9·01, or has become 0·74 smaller; and hence for *one degree* the change amounts to $\frac{0{\cdot}74}{55}$, or 0·0134, and the equivalent volume of carbon in a compound, at D° below its boiling-point, is expressed by the formula, $(C) = 8 \times (9{\cdot}75 - D \times 0{\cdot}0134)$; and the equivalent volumes of hydrogen and oxygen by the formula (H) and $(O) = 6 \times (9{\cdot}72 - D \times 0{\cdot}0134.)$

From the equivalent volume of alcohol at the boiling-point and at 3°·4, we calculate that the number by which D must be multiplied to express the change of the constant factor is 0·0108.

The boiling-point of alcohol is 78°·4, and the equivalent volume, calculated according to the formula $C_4 H_6 O_2$, is 782, or $4 \times 78 + 6 \times 58{\cdot}5 + 2 \times 58{\cdot}5$; at 3°·4 (D is consequently in this case 75°), the equivalent volume is 715·5. From a mean of these and other observations, Kopp determines this magnitude at 0·01, and hence the equivalent volumes in which carbon, hydrogen, and oxygen are contained in a compound at D° below the boiling-point, are expressed by

$$(C) = 8 \times (9{\cdot}75 - 0{\cdot}01\ D)$$
$$(H) = 6 \times (9{\cdot}75 - 0{\cdot}01\ D)$$
$$(O) = 6 \times (9{\cdot}75 - 0{\cdot}01\ D)$$

In a compound which boils at 80° the equivalent volume of carbon at 60° (or 20° below the boiling-point) $= 8 \times (9{\cdot}75 - 20 \times 0{\cdot}01) = 8 \times 9{\cdot}55 = 76{\cdot}4$; in a compound which boils at 137°, the equivalent volume of oxygen at $13° = 51{\cdot}06$. D is therefore in this case $137° - 13° = 124°$, and hence we have $6 \times (9{\cdot}75 - 124 \times 0{\cdot}01)$. Hence, generally, the equivalent volume of a liquid compound consisting of a equivalent of carbon, b of hydrogen, and c of oxygen, at a temperature which is D° from the boiling-point of the compound is

$$(8a + 6b + 6c) \times (9{\cdot}75 - 0{\cdot}01\ D)$$

The following illustrations tend to show how far this formula gives results coinciding with those yielded by observations.

Let us calculate the equivalent volume and the specific gravity of carbonic ether for 19°. Carbonic ether boils at 126°; D is therefore in this case $=126°-19°=107°$. As carbonic ether is expressed by the formula $C_5 H_5 O_3$, its equivalent volume at 19° must be, according to the above formula,

$(5\times 8+5\times 6+3\times 6)\times(9{\cdot}75-0{\cdot}01\times 107°)=88\times 8{\cdot}68=764$

and since the equivalent weight is 737·5 the specific gravity at $19°=\frac{737{\cdot}5}{764}=0{\cdot}97$. Ettling has found it to be 0·975.

For hydrated caryophyllic acid, $C_{20} H_{12} O_4$, whose equivalent is therefore 2050, and whose boiling-point is 243°, the above formula gives the specific gravity 1·08 at 8° C., while Ettling actually found it to be 1·079.

If one of the three elements is altogether absent in the compound we must proceed as if there were 0 equivalents present. A compound, $C_2 H$, which boils at 85°, has at 15° the equivalent volume $(2\times 8+6)\times(9{\cdot}75-0{\cdot}01\times 70)=199$; and since the equivalent is 162·5, the specific gravity at 15° is $\frac{162{\cdot}5}{199}$, or 0·82. Kopp has not only endeavoured to determine the equivalent volumes of carbon, hydrogen, and oxygen, but also of chlorine, nitrogen, and sulphur.

In relation to these various points I must refer to page 98 of his excellent memoir, and will only add that the following values correspond the best with the results of actual observation.

$$(Cl) = 28\times(9{\cdot}75-0{\cdot}01\,D)$$
$$(N) = 18\times(9{\cdot}75-0{\cdot}01\,D)$$
$$(S) = 15\times(9{\cdot}75-0{\cdot}01\,D)$$

In order to facilitate the calculations, the equivalent volumes which are assumed for C, H, O, Cl, N, and S, in a liquid compound at a temperature of D° below the boiling-point, have been collected by Kopp into a table which I here transcribe without changing the old equivalent weights of Cl, N, and S.

D	C Equiv. 75.	H and O Equiv. = 12·5. Equiv. = 100.	Cl Equiv. = 442·6.	N Equiv. = 176.	S Equiv. = 201.
0	78·0	58 5	273	175·5	146·25
10	77·2	57·9	270·2	173·7	144·75
20	76·4	57·3	267·4	171·9	143·25
30	75·6	56·7	264·6	170·1	141·75
40	74·8	56·1	261·8	168·3	140·25
50	74·0	55·5	259·0	166·5	138·75
60	73·2	54·9	256·2	164·7	137·25
70	72·4	54·3	253·4	162·9	135·75
80	71·6	53·7	250·6	161·1	134·25
90	70·8	53·1	247·8	159·3	132·75
100	70·0	52·5	245·0	157·5	131·25
110	69·2	51·9	242·2	155·7	129·75
120	68·4	51·3	239·4	153·9	128·25
130	67·6	50·7	236·6	152·1	126·75
140	66·8	50·1	233·8	150·3	125·25
150	66·0	49·5	231·0	148·5	123·75
160	65·2	48·9	228·2	146·7	122·25
170	64·4	48·3	225·4	144·9	120·75
180	63·6	47·7	222·6	143·1	119·25
190	62·8	47·1	219·8	141·3	117·75
200	62·0	46·5	217·0	139·5	116·25
210	61·2	45·9	214·2	137·7	114·75
220	60·4	45·3	211·4	135·9	113·25
230	59·6	44·7	208·6	134·1	111·75
240	58·8	44·1	205·8	132·3	110·25
250	58·0	43·5	203·0	130·5	108·75
260	57·2	42·9	200·2	128·7	107·25
270	56·4	42·3	197·4	126·9	105·75
280	55·6	41·7	194·6	125·1	104·25
290	54·8	41·1	191·8	123·3	102·75
300	54·0	40·5	189·0	121·5	101·25

The application of this table hardly requires explanation. Let us suppose, by way of illustration, that we employ it to determine the specific gravity of chlorobenzide (Mitscherlich) at 7° C. Chlorobenzide is $C_{12} H_3 Cl_3$; its equivalent is 2265; its boiling-point is 210° C., and hence $D = 210 - 7$, or 203. If, for the sake of convenience, we make $D = 200$, we calculate the equivalent volume as $12 \times 62 + 3 \times 46{\cdot}5 + 3 \times 217$, or 1534·5, and if we divide the equivalent weight by the equivalent volume we obtain for a quotient 1·476 as the specific gravity. Mitscherlich found it at the given temperature, 7° C., to be 1·457. Or, suppose we have to calculate the specific gravity of mercaptan at 21° C. Mercaptan, the hydrosulphide of the sulphide of ethyl, is represented by the formula $C_4 H_6 S_2$, and its

equivalent is 777; its boiling-point has been fixed by Liebig at 36°·2 C. In this case D is 36°·2 − 21°, or 15°·2 C. If D = 15 the equivalent volume of mercaptan is $4 \times 76{\cdot}8 + 6 \times 57{\cdot}6 + 2 \times 144 = 941$; and if we divide the equivalent weight by this number we obtain 0·826 as the calculated specific gravity, while Liebig actually found it to be 0·835.

To this table Kopp appends several interesting remarks. He thinks that it may be assumed with equal probability that the equivalent volumes which pertain to the elements in combination are the same as those elements possess in an isolated state; for instance, that sulphur in a liquid combination at 100° below the boiling-point is contained in the same equivalent volume which it has when isolated, in a liquid state, at 100° below *its* boiling-point. If we have already found that the elements when in combination have a different equivalent volume from that which they have in an isolated state, we must to this condition add that the equivalent volumes of the elements are not determined for corresponding temperatures. It is very probable, according to Kopp, that for solid bodies those temperatures are approximatively corresponding which are equally distant from the fusion-point. We say, for instance, that the equivalent volume of potassium in combination, as in its sulphates, is different from that which we observe for potassium in the isolated state, since the equivalent volume of sulphate of potash is smaller than that of potassium. We have not at present the means of accurately determining this point, since we are only acquainted with the equivalent volumes of potassium and its compounds at mean temperatures. In all probability the equivalent volume of potassium is the same in combination as in its isolated state, for equal distances from the fusion-points. If we could observe the equivalent volume of potassium at a degree of temperature which is as far distant from the fusion-point of this metal as the difference of temperature between the fusion-point of sulphate of potash and the temperature at which we observe the equivalent volume of this salt, we should find that the equivalent volume of potassium is much smaller than that of the salt, while the observations which are instituted for one and the same, for the mean temperature, give the very reverse. The

equivalent volume which we assign to potassium in its sulphates, and which is different from that which it has been observed to have in its free state, will approximate to that which the potassium possesses at a degree of temperature as far distant from its fusion-point as the temperature of the fusion-point of sulphate of potash is from the temperature at which the specific gravity of the salt was observed. According to Kopp strong objections may be brought against this mode of observation, which cannot be removed until the fusion-point and the expansion of many inorganic substances have been accurately determined.

If the formula that we have given for the calculation of the equivalent volumes of C, H, O, Cl, N, and S at equal distances from the boiling-point of their compounds were absolutely correct in regard to their form, and in reference to all the numerical calculations contained in it, it might then, in addition to its principal object, also serve, by the known atomic composition and a specific gravity observation at a known temperature, to lead to the determination of the distance of the observed temperature from the boiling-point, or, in other words, of the boiling-point. But since the formula cannot be regarded as undoubtedly certain, and the estimation of the numbers contained in it is not altogether to be depended on, it would be a matter of considerable hazard to attempt to determine the boiling-point by this means. (Kopp.) The reasons of the uncertainty of the formula are thus explained by Kopp. The form of the formula depends on the assumption: (1) that the equivalent volumes which are taken for C, H, O, Cl, N, and S in liquid combinations, always stand in the same relations to one another at corresponding temperatures. This assumption is certainly the simplest, but still it is a perfectly arbitrary one; (2) that those should be regarded as corresponding temperatures which are equally distant from the boiling-point. This assumption, as far as actual practice is concerned, gives results which, in most cases, approximate pretty closely with the truth, but, strictly speaking, it is not correct, and consequently leads to false theoretical results, as may be seen by the following remarks.

According to the formula the contraction which a liquid

undergoes on cooling x° from the boiling-point, is always proportional to the magnitude x. Experience, however, most decidedly shows us that in by far the greater number of liquids this is not the case; for a definite interval of temperature the contraction is almost always smaller, the more distant this is from the boiling-point. Moreover, according to the formula, all liquids, if we assume for them equal volumes at the boiling-point, at equal distances from the boiling-point occupy equal volumes. If we assume that the volume of any liquid at its boiling-point is 9·75, then at a distance of D° from the boiling-point it will be $9{\cdot}75 - 0{\cdot}01D$. Moreover this conclusion is not confirmed by experience, but is much oftener opposed by it, if, for the numerical determination 9·75 and 0·01, other magnitudes are assumed as more correct.

That the numerical determinations in the formula are uncertain is a fact not concealed by Kopp, in various parts of the treatise to which we have so often referred; he adds, in relation to the point, the assumption that the equivalent volume of hydrogen is equal to that of oxygen, the basis of all our determinations, is far from being so confirmed by direct observations as to be regarded entirely accurate; it is possible that the relation of the equivalent volumes is nearly, without being perfectly, the same, just as in the estimation of the equivalents of elements simple relations are often tolerably approximative, but after the most accurate determinations are not positively correct.

The practical applicability of the formula appears from a large number of results to be well established. The formula gives the specific gravity of liquid compounds for any distance of temperature from the boiling-point with an accuracy that deserves attention.

Aubergier has ascertained empirically that the volatile oils isomeric (polymeric) with oil of turpentine have the same specific gravity at temperatures equally distant from their boiling-points. The formula leads to the same result, since it requires that all liquid substances of equal empirical atomic construction (an equal per-centage composition) should have the same specific gravity at temperatures equally distant from the boiling-point. Hence, at the ordinary temperatures at

which observations are made, the specific gravity of polymeric substances boiling at high temperatures must be greater than that of those with lower boiling-points.

The formula may also serve for the estimation of the density of the vapours of a compound. The latter is done in order to obtain a check in ascertaining the relation in which the atoms of the elements unite to form a compound, and at the same time as a means of knowing how many elementary atoms are contained in *one* atom of the compound. Our formula, in its present state, can only be used as a check.

In addition to the knowledge of the atomic relations in which the elements unite to form a combination, the determination of the boiling-point is sufficient to enable us to calculate the specific gravity of the liquid, and the observation with which this calculation is compared is easily and simply made. But the formula also affords the means of ascertaining the atomic weight of a liquid compound and of determining how many elementary atoms are embraced in *one* atom of the compound, if the magnitudes contained in it are so accurately determined, that the boiling-point enables us indirectly to ascertain the composition, and the density at a given temperature. Löwig believes that it may be mathematically demonstrated, (1) that the values assumed by Kopp as the equivalent volumes of carbon, hydrogen, and oxygen, in liquid organic compounds are false, and (2) that the equivalent volume of an element is not, as Kopp believes, equally great in all combinations. (*Pogg. Annal.*, 1846, Bd. lxviii., s. 51, &c.) We have already mentioned that the compound molecule $C_2 H_2$ has in its combinations a constant equivalent volume, which, if we compare the equivalent volumes of the ethyl and methyl compounds without reference to correspondence of temperature, amounts to about 234. If we take, as a foundation, the equivalent volumes established by Kopp for carbon and hydrogen in combinations at their boiling-points, namely 78 and 58·5, the equivalent volume of this compound molecule is $2 \times 78 + 2 \times 58{\cdot}5$, or 273. Löwig now ascertains the equivalent volume of $C_2 H_2$ directly for the boiling-point, by establishing a comparison between the combinations which differ in their composition by $C_2 H_2$, or by a multiple of it, in reference to their

equivalent volume at the boiling-point, and arrives at discrepant results. Since the contraction that occurs on cooling is not accurately established for other liquids here to be considered, as it is for water, alcohol, and ether, he compares, in this point of view, the compound ethers, wood spirit, and fousel oil with alcohol, but acetone and the simple oxides with ether*, in order to calculate the equivalent volumes for the boiling-point. The following table contains the data for these comparisons:

		Spec. Grav.	Below the Boiling point.	Equiv. Vol. Atomic Vol.
Ether	$C_4 H_5 O$	0·6974	0°	663
Acetone	$C_2 H_3 O$	0·925	37°	458
Alcohol....	$C_4 H_6 O_2$	0·739	0°	780
Formiate of oxide of ethyl	$C_6 H_6 O_4$	0·9085	34°	1018
Acetate of oxide of ethyl	$C_8 H_8 O_4$	0·890	59°	1236
Wood-spirit	$C_2 H_4 O_2$	0·7938	40°	503
Fousel oil	$C_{10} H_{12} O_2$	0·8137	118°	1351
Valerianate of oxide of methyl,	$C_{12} H_{12} O_4$	0·8806	100°	1646

If now we proceed to calculate the equivalent volumes of these compounds for the boiling-point in accordance with the contraction of alcohol, we obtain the following values:—

		Equiv. Volume.
Ether	$C_4 H_5 O$	663
Acetone	$C_2 H_3 O$	480
Alcohol	$C_4 H_6 O_2$	780
Formiate of oxide of ethyl....	$C_6 H_6 O_4$	1073
Acetate of oxide of ethyl	$C_8 H_8 O_4$	1323
Wood-spirit	$C_2 H_4 O_2$	528
Fousel oil	$C_{10} H_{12} O_2$	1529
Valerianate of oxide of methyl	$C_{12} H_{12} O_4$	1832

If we subtract the equivalent volume of one of these compounds from that of another differing from it by $C_2 H_2$, or some multiple of $C_2 H_2$, the difference naturally indicates the equivalent with which $C_2 H_2$, $2C_2 H_2$, &c., are contained in the latter compound. For instance:

* According to Gay-Lussac the following diminution occurs in 1000 parts :—

	Water.	Alcohol.	Ether.
From 0° to 15° from the boiling-point downwards	10·50	17·51	24·23
„ 15° to 30° „ „	8·35	17·23	22·09
„ 30° to 45° „ „	7·65	16·11	19·06
„ 45° to 60° „ „	5·92	15·11	
„ 60° to 75° „ „	4·26	14·15	

Equiv. Vol.

Alcohol .... $C_4 H_6 O_2 = 780$
Wood-spirit .... $C_2 H_4 O_2 = 528$ $C_2 H_2 = 252$

$C_2 H_2 = 252$

Valerianate of oxide of methyl $C_{12} H_{12} O_4 = 1832$
Acetate of oxide of ethyl .... $C_8 H_8 O_4 = 1323$ $C_2 H_2 = \frac{509}{2} = 254$

$C_4 H_4 = 509$

Fousel oil .... $C_{10} H_{12} O_2 = 1529$
Alcohol .... $C_4 H_6 O_2 = 780$ $C_2 H_2 = \frac{749}{3} = 250$

$C_6 H_6 = 749$

Fousel oil .... $C_{10} H_{12} O_2 = 1529$
Wood-spirit .... $C_2 H_4 O_2 = 528$ $C_2 H_2 = \frac{1001}{4} = 250$

$C_8 H_8 = 1001$

Hence, in this manner we obtain for $C_2 H_2$, the constant volume 250, while, according to Kopp, it amounts to 273. Assuming that the former number is the correct one, we obtain for H O the following volumes:

Equiv. Vol.

Alcohol .... $C_4 H_6 O_2 = 2C_2 H_2 + 2HO = 780$
$- 2C_2 H_2 = 500$ $HO = \frac{280}{2} = 140$

$2HO = 280$

Wood-spirit.... $C_2 H_4 O_2 = C_2 H_2 + 2HO = 528$
$- C_2 H_2 = 250$ $HO = \frac{278}{2} = 139$

$2HO = 278$

Fousel oil .... $C_{10} H_{12} O_2 = 5C_2 H_2 + 2HO = 1529$
$- 5C_2 H_2 = 1250$ $HO = \frac{279}{2} = 139{\cdot}5$

$2HO = 279$

For the equivalent volume of oxygen we obtain the following values:

Equiv. Vol.

Acetate of oxide of ethyl .... $C_8 H_8 O_4 = 4C_2 H_2 + O_4 = 1323$
$-4C_2 H_2 = 1000$ $O = \frac{323}{4} = 80{\cdot}8$

$O_4 = 323$

Formiate of oxide of ethyl .... $C_6 H_6 O_4 = 3C_2 H_2 + O_4 = 1073$
$-3C_2 H_2 = 750$ $O = \frac{323}{4} = 80{\cdot}8$

$O_4 = 323$

Equiv. Vol.

Valerianate of oxide of methyl $C_{12}H_{12}O_4 = 6C_2H_2 + O_4 = 1832$

$-6C_2H_2 = 1500$ $O = \frac{332}{4} = 83$

$O_4 = 332$

Kopp's values, however, are, for water 117, and for oxygen 58·5. Such coincident results for the volumes of C_2H_2, HO, and O, as are given above are, however, according to Löwig, only obtained when we happen to institute comparisons between compounds with similar rational formulæ. If we compare combinations of different rational formulæ, we obtain different values; thus—

Equiv. Vol.

Fousel oil .... $C_{10}H_{12}O_2 = 1529$

Acetate of oxide of ethyl .... $C_8H_{10}O_2$* $= 1323$

$C_2H_2 = 206$ instead of 250

2 eq. Ether .... $C_8H_{10}O_2 = 1326$

1 eq. Wood-spirit .... $C_2H_4O_2 = 528$ $C_2H_2 = \frac{798}{3} = 266$

$C_6H_6 = 798$

Ether .... $C_4H_5O = 2C_2H_2 + HO = 663$

$-2C_2H_2 = 500$

$HO = 163$ instead of 117

Acetone .... $C_3H_3O = 1\frac{1}{2}C_2H_2 + O = 480$

$-1\frac{1}{2}C_2H_2 = 375$

$O = 105$ instead of 80·8

If we subtract the equivalent volume of ether (663) from the equivalent volume of alcohol (780), there remains the number 117 (already determined) for HO. If, from the formula for alcohol $2C_2H_2 + HO$, we subtract 500, as the number for C_4H_4, there remains, as has been already shown, 280 for 2HO. If the volumes of the equivalents of oxygen and hydrogen were equal, they must amount to 2×117, or 234. But $280 - 117 = 163$, and, as we have clearly seen, HO actually occurs in ether with the volume 163. Hence, according to

* Since, according to Kopp, hydrogen and oxygen have an equal equivalent volume, O may be arbitrarily substituted for H. The formula for acetic ether, $C_8H_8O_4$, is in this way converted into $C_8H_{10}O_2$.

Löwig, it is completely proved that if we separate alcohol into $2C_2H_2+2HO$, the one equivalent of water must occur in the compound with the volume 117, and the other with the volume 163.

If we assume that the equivalent volume of H is represented by 58·5, and C_2H_2 is taken as equal to 250, we obtain for C the volume 66·5 in place of 78, for $250-117=133$, and $\frac{133}{2}=66{\cdot}5$.

On comparing with one another the compounds which have different rational formulæ we obtain for C and H the most discrepant values.

	Equiv. Vol.	
Ether	$C_4H_5O = 663$	
−Wood-spirit	$C_2H_4O_2 = 528$	$C = \frac{135}{2} = 67{\cdot}5$
	$C_2 = 135$	
Alcohol	$C_4H_6O_2 = 780$	
−Acetone	$C_3H_3O = 480$	
	$CH_3O = 300$	
	$-H_3O = 234$	$C = 66$
	$C = 66$	
4 equiv. Acetone	$C_{12}H_{12}O_4 = 1920$	
−1 equiv. Fousel oil	$C_{10}H_{12}O_2 = 1529$	
	$C_2 \quad O_2 = 391$	$C = \frac{274}{2} = 137$
	$-O_2 = 117$	
	$C_2 = 274$	
4 equiv. Acetone	$C_{12}H_{12}O_4 = 1920$	
−1 equiv. Acetic ether	$C_8H_8O_4 = 1323$	
	$C_4H_4 = 597$ instead of 500	
	$-H_4 = 234$	$C = \frac{362}{4} = 90$
	$C_4 = 363$	
4 equiv. Acetone	$C_{12}H_{12}O_4 = 1920$	
−1 equiv. Formic ether....	$C_6H_6O_4 = 1073$	
	$C_6H_6 = 847$ instead of 750	
	$-H_6 = 351$	$C = \frac{496}{6} = 82$
	$C_6 = 496$	

		Equiv. Vol.	
Fousel oil	.... $C_{10} H_{12} O_2$	= 1529	
−2 eq. Acetone	.... $C_6 H_6 O_2$	= 960	
	$C_4 H_6$	= 569	$H = \frac{69}{2} = 34{\cdot}5$
	$-C_4 H_4$	= 500	
	H_2	= 69	
3 equiv. Ether....	.... $C_{12} H_{14} O_4$	= 1989	
−Valerianic ether	.... $C_{12} H_{12} O_4$	= 1832	$H = \frac{157}{2} = 78{\cdot}5$
	$H_2 O_4$	= 157	

The illustrations already adduced are sufficient, according to Löwig, to establish the fact that Kopp's values are not correct, and that the volumes of an elementary atom cannot be equally great in all compounds. It is, however, equally well proved that this is based upon regular laws, since otherwise we could not always obtain, for a series of cases, the numbers 250 for $C_2 H_2$, 280 for 2H O, and 80·8 for O.

The fact, that the specific gravity of the carburetted hydrogen generally remains nearly constant, however much the proportion of the equivalents (atoms) of carbon and hydrogen may differ, and that the specific gravity is always considerably increased if only a few equivalents of oxygen are combined with it, suggested to Löwig the idea that the specific gravities of carbon and hydrogen in organic compounds might be equal. In order to put this idea to the test, he compared the combinations belonging to one group, as, for instance, alcohol, ether, acetic acid, and acetone; wood spirit and formic acid; fousel oil and valerianic acid; oil of bitter almonds and benzoic acid. Ether and acetone were first compared.

Equivalent volume of ether	....	$C_4 H_5 O = 663$
„ acetone	....	$C_3 H_3 O = 480$
		$C H_2 = 183$

If now the specific gravity of carbon is the same as that of hydrogen, then must $\frac{6}{8}$ of the volume 183 be carbon, and $\frac{2}{8}$ hydrogen (in $C H_2$, 2 parts by weight of H occur with 6 parts by weight of C). If we take the equivalent atom of hydrogen (=12·5) as our unit, then $C H_2 = 8$ units (since $8 \times 12{\cdot}5 = 100$

parts by weight). The space occupied by the unit of weight (12·5) is therefore found on dividing 183 by 8, and =22·87.

Ether contains 24 units by weight of carbon and 5 of hydrogen, =29, and acetone contains 18 of carbon and 3 of hydrogen, =21.

If we multiply the unit of space (22·87) by 29 and 21 we obtain the exact equivalent volumes of ether and acetone:

$$29 \times 22{\cdot}87 = 663, \text{ and } 21 \times 22{\cdot}87 = 480$$

which proves, according to Löwig, that the equivalent volumes of ether and acetone are equal to the space which belongs to their radicals, and that a condensation occurs which is equal to the equivalent volume of oxygen. 1 equivalent volume of ether (663) + 1 equivalent volume of water (117) is equal to the equivalent volume of alcohol (=780). Now wood-spirit and fousel oil have a similar chemical constitution to alcohol. On subtracting 117 for H O from the equivalent volume of these combinations, we obtain the equivalent volume for oxide of methyl, $C_2 H_3 O$, and for oxide of amyl, $C_{10} H_{11} O$.

The equiv. vol. of wood-spirit = 528	The equiv. vol. of fousel oil = 1529
„ for H O = 117	„ for H O = 117
$C_2 H_3 O = 411$	$C_{10} H_{11} O = 1412$

In accordance with ether and acetone the space 411 must correspond to the volume of $C_2 H_3$, and the space 1412 to the volume of $C_{10} H_{11}$. Now, $\frac{411}{22{\cdot}87} = 18$ units of space, and $\frac{1412}{22{\cdot}87} = 62$ U. S. But $C_2 H_3 = 15$ units of weight, and $C_{10} H_{11} = 71$ U. W.; hence, in methyl 15 U. W. = 18 U. S., and in amyl 71 U. W. = 62 U. S.

Hence, in methyl there are 3 more units of space than there are units of weight. Methyl contains 3 eq., and, according to Löwig, it is, at all events, most simple to assume (and indeed any other assumption would be impossible) that in methyl the equivalent volume of hydrogen is as large again as in ether and acetone. If we suppose that this expansion of the hydrogen also takes place in fousel oil it follows that the volume of the carbon in fousel oil is one-third more condensed than in ethyl or methyl. Hence we obtain:

C_2	=	12 u s	C_{10}	=	40 u s
H_3	=	6 „	H_{11}	=	22 „
O	=	0 „	O	=	0 „
$C_2 H_3, O$	=	18 „	$C_{10} H_{11}, O$	=	62 „

Hence the volumes of the atoms of carbon and hydrogen are to one another in ethyl as 6 : 1; in methyl as 3 : 1, and in amyl as 2 : 1; and if it is assumed that in methyl the atoms of carbon and hydrogen are in their normal state, and if, for the unit of space, we take 22, as a number easily divisible, then—

(1.) The atom-volume of hydrogen = 44
(2.) „ „ carbon = 132

And the condensations are—

$\frac{1}{2}$ for the hydrogen atom = 22 = 1 atom-volume*
$\frac{1}{3}$ „ carbon atom = 88 = 1 atom-volume

With 6 and 4 units of space for the equivalent of carbon, and 2 and 1 for the equivalent of hydrogen, the calculated specific gravity, according to Löwig, exactly accords with the result of experiment, if we base it upon Gay-Lussac's contraction. According to him it is so far mathematically established that the elements in combinations have different volumes.

According to Löwig, alcohol and the acetic hydrate have an equal equivalent volume, and so also have wood spirit and the formic hydrate, and fousel oil and the valerianic hydrate. Since, in the formation of acetic acid by the oxidation of alcohol, when 2 atoms of hydrogen are abstracted from the ether of the alcohol, the remaining atoms do not change their volume, the condensed atom of oxygen remains unaltered. From $C_4 H_5 O$ (ether) we have $C_4 H_3 O$ (oxide of acetyl). But on oxidizing $C_4 H_3 O$ to $C_4 H_3 O_3$, that is to say, to acetic acid, this additional atom of oxygen corresponds to 1 unit of space.

C_4	=	24 u s	C_4	=	24 u s
H_5	=	5 „	H_3	=	3 „
O	=	0 „	O	=	0 „
Ether	=	29 „	Oxide of acetyl	=	27 „

* In some combinations the condensation $\frac{2}{2}$ (= 33,) also occurs. (*Pogg. Ann.*, bd. lxiv. s. 292.)

Oxide of acetyl	=	27 u s
O_2	=	2 „
Acetic acid	=	29 „

If this oxidation takes place in compounds in which the atom-volume of hydrogen = 2 u. s, the atom of oxygen which enters the compound corresponds to 2 u. s.

C_2	=	12 u s
H_3	=	6 „
O	=	0 „
Oxide of methyl	=	18 „

C_2	=	12 u s
H	=	2 „
O	=	0 „
O_2	=	4 „
Formic acid	=	18 „

It follows from the laws of gaseous combinations that the gaseous oxide of ethyl unites without condensation with the organic acids, as with the vapour of water, and coinciding with the combination of liquid oxide of ethyl with water; there doubtless occurs the same relation in the union of the liquid oxide of ethyl with the liquid acids, an assumption which is in all respects confirmed by the specific gravity of this compound.

The specific gravity of acetate of oxide of ethyl at 64°, or 10° below its boiling-point, is 0·840, and consequently its equivalent volume is $\frac{1100}{0{\cdot}840}$, or 13·10. In accordance with Gay-Lussac's contraction for alcohol at 10° below the boiling-point, the unit of space has the volume 22·62, and hence we calculate for acetic ether the unit of space $= \frac{1310}{22{\cdot}62} = 58$ u. s. The sum of the unit of space is then (29) for ether, and (29) for acetic acid*.

If we assume for water 5 units of space, which certainly is not exactly accurate, since $5 \times 22{\cdot}87 = 114$ instead of 117, then, according to Löwig, these correspond to the equivalent volume of

Alcohol	C_4H_5O,HO	.... 34 u s and	$\frac{790}{34} = 22{\cdot}87$
Ether	C_4H_5O	.... 29 „ and	$\frac{663}{29} = 22{\cdot}87$
Acetone	C_3H_3O	.... 21 „ and	$\frac{480}{21} = 22{\cdot}80$

* I will remark that we should reckon 16 units of space instead of 18 for the formic acid calculated from formic ether. (Löwig, *Pogg. Annal.*, 64, s. 516.)

Formic ether	E O, Fo O_3	.... 47 u s	and $\frac{480}{47}$	= 22·83
Acetic ether	E O, $\bar{A}$	.... 58 „	and $\frac{1323}{58}$	= 22·81
Wood-spirit	Me O, H O	.... 23 „	and $\frac{528}{23}$	= 22·83
Fousel oil	Am O, H O	.... 67 „	and $\frac{1529}{67}$	= 22·73
Valerianate of oxide of methyl	Me O, Va O_3	.... 80 „	and $\frac{1832}{80}$	= 22·81

The volume of the unit of space is therefore found experimentally to be of perfectly equal size.

The following paragraphs contain the laws which Löwig has established for the relations of volume in the combinations of C, H, and O and the radicals consisting of C and H, together with the nomenclature he has formed for them, by which these laws may be generally expressed:

(1.) The radicals consisting of carbon and hydrogen he divides into two classes:

(*a*) Into hydroisocarbonyles, or radicals which contain either an equal number of atoms of carbon and hydrogen, or in which one element exceeds the other by one atom.

(*b*) Into hydropolycarbonyles, in which the atoms of carbon exceed those of hydrogen.

(2.) The Hydroisocarbonyles are divisible, according to the relation of the atoms of carbon and hydrogen, into

(*a*) Dyhenyles, or radicals containing one atom more of carbon than of hydrogen, C_2H, C_4H_3, C_6H_5.

(*b*) Perisyles, or radicals which consist of an equal but odd number of atoms of carbon and hydrogen, as CH, C_3H_3, C_7H_7.

(*c*) Diotryles, or radicals in which there is one more atom of hydrogen than of carbon, C_2H_3, C_4H_5, $C_{10}H_{11}$.

(*d*) Artyles, or radicals consisting of an equal and even number of atoms of carbon and hydrogen, C_2H_2, C_4H_4.

(3.) Associated radicals belonging to the same groups form an ascending series, in which each term contains C_2H_2 more than its predecessor, and the collective terms of a group agree with one another in their elementary properties.

(4.) The Dyhenyles unite with 3 at. of oxygen to form organic acids: C_2H, O_3, C_4H_3, O_3, C_6H_5, O_3. The Dyotryles form oxides with one atom of oxygen, which comport themselves as bases. The acids of the dyhenyles unite with the

oxides of the dyotryles, and both unite with one at. of water to form hydrates.

(5.) If we distinguish by the symbols A_1, A_2, A_3, &c., the terms 1, 2, 3, &c., of the series of acids formed by the union of a dyhenyle with 3 at. of oxygen, or C_2H, O_3, C_4H_3, O_3, C_6H_5, O_3; and likewise by the symbols B_1, B_2, B_3, &c., the corresponding oxides of a dyotryle, or C_2H_3, O, C_4H_5, O_3, and by 1, 2, 3, &c., the hydrates of the dyhenyle acids, or $C_2H, O_3 + HO$, $C_4H_3, O_3 + HO$; it follows from the relation of the atoms of carbon and hydrogen, that the combinations $A_1 + B_1$ must have the same elementary composition as the acid hydrate 2; and, generally, we obtain the following series of metameric combinations.

$$A_1 + B_1 = 2$$
$$A_2 + B_1 = A_1 + B_2 = 3$$
$$A_3 + B_1 = A_2 + B_2 = A_1 + B_3 = 4$$
$$A_4 + B_1 = A_3 + B_2 = A_2 + B_3 = A_1 + B_4 = 5$$
$$\&c., \&c.$$

(6.) The atom-volume of hydrogen is to that of carbon in the

First term	....	C_2H, C_2H_3, C_2H_2	as 2 : 6
Second term	....	C_4H_3, C_4H_5, C_4H_4	as 1 : 6
Higher term	....	C_8H_7, $C_{10}H_{11}$, $C_{10}H_{10}$	as 2 : 4

If the weight of the unit of weight = 12·5 then is
The volume of the unit of space = 22·87 at the boiling-point, and the
Specific gravity of the unit of space = $\frac{12·5}{22·87}$ = 0·546 at the boiling-point.

(7.) If we combine the hydroisocarbonyles with 1 at. of oxygen, there takes place a condensation equal to an atom-volume of oxygen. Hence, the volume of the radical, when combined with 1 at. of oxygen, remains unchanged, whilst an augmentation of the specific gravity corresponding to a unit of weight of oxygen ensues. If, however, the oxides of the dyhenyles take up 2 atoms of oxygen, the volume of these atoms of oxygen is equal to the volume of the atoms of hydrogen in the compound. Consequently the atom-volume of oxide of ethyl, C_4H_5O, is equal to the atom-volume of acetic acid, $C_4H_3O_3$; and the atom-volume of oxide of amyl, $C_{10}H_{11}O$, is equal to the atom-volume of valerianic acid,

$C_{10} H_9 O_3$. *Hence it follows generally that the dyotryles, their protoxides, and the dyhenyle acids, formed from these oxides with* 3 *at. of oxygen, have equal atom-volumes.*

(8.) If the acids and oxides of the hydroisocarbonyles combine with 1 atom of water to form hydrates, the atom-volume of the compound corresponds with the atom-volume of the constituents; and hence, at the boiling-point the increase of volume amounts to 117. *In the conversion of wood spirit into the hydrate of formic acid, of alcohol into the hydrate of acetic acid, and of amylic alcohol (fousel oil) into the hydrate of valerianic acid, there is consequently no change in the atom-volume.*

(9.) If the dyhenyle acids combine with the oxides of the dyotryles, then also is the atom-volume of the compound equal to the atom-volume of the constituents. Since in methyl and in ethyl the atom-volume of the hydrogen, and in amyl that of the carbon also is different, it follows that the atom-volume of metameric compounds of methyl, ethyl, and amyl cannot exactly coincide with one another. Formiate of oxide of ethyl and acetate of oxide of methyl, valerianate of oxide of ethyl and acetate of oxide of amyl, are the only compounds of this nature which have, on these grounds, an equal atom-volume.

The equivalent or atom-volume of chlorine is fixed by Löwig at 10·5 units of space from observations ranging between 8 and 10, (*Pogg. Annal.*, bd. 64, s. 527,) 36 U. W. are therefore 10·5 U. S., and he thinks that we may assume that 36 U. W. have become condensed to $\frac{1}{3 \cdot 5}$ the original bulk.

The specific gravity of perchloride of formyl (chloroform), at 40° C. below its boiling-point, is 1·48, and since the atomic weight is 1490, the atomic volume is $\frac{1490}{1 \cdot 48}$, or 1007, and $\frac{1007}{21 \cdot 8} = 46$ units of space.

Now C_2	$= 2 \times 6$	$= 12$ units of space
H	$= 1 \times 2$	$= 2$ „
Cl_3	$= 3 \times 10 \cdot 5$	$= 32$ „
$C_2 H Cl_3$		$= 46$ units of space

For the atomic volume of iodine, as determined from iodide of ethyl, Löwig obtains 17·46 units of space, and for the atomic volume of bromine, as determined from the bromide of ethyl,

13·8 units of space, and the latter is exactly the mean of the atomic volumes of chlorine and iodine. The atomic volume of sulphur he calculates at 2 U. S. and 8 U. S., and that of nitrogen at 7 U. S.

Rhodanethyl (sulphocyanide of ethyl), E Rn, or E, $C_2 N S_2$, has at 15° C*., that is to say, 80° below its boiling-point, the same specific gravity as water; hence, as the atomic weight is 1087·5, the atomic volume is $\frac{1087·5}{1}$, or also equal to 1087·5, which yields $\frac{1087·5}{20·8}$, or 52 units of space.

Now C_2	$= 2 \times 6 =$	12 units of space
S_2	$= 2 \times 2 =$	4 „
N	$=$	7 „
E	$=$	29 „
$E C_2 N S_2$	$=$	52 units of space

From all these experiments Löwig finally draws the conclusion: that 1, the atomic volumes of organic combinations stand in a simple relation to their atomic weights. 2. That the normal relations exhibited by organic combinations in their gaseous condition, are only the result of the normal molecular conditions of solid and liquid combinations.

Time must decide upon the importance of Löwig's laborious work. He has further developed what Schröder had previously established regarding the atomic volumes of solid compounds, namely, that the constituent or ultimate elements of the latter are contained with a different atomic volume. All the calculations of Löwig rest upon the hypothesis that liquid organic compounds are expanded by heat in the same manner as alcohol; and it is therefore singular that the tenability of these views has not been in any degree investigated.

I cannot leave the subject of the connection between the equivalents and the volume of bodies in a solid and liquid condition without making mention of a few ingenious suggestions by Schröder on the relations which, according to this chemist, exist between the equivalent volume and some few other properties of bodies. Solid and liquid bodies are, as is well known, not equally expanded by heat.

* The volume of the unit of space at 80° to 90° below the boiling-point.

On calculating the expansion of the elements for their equivalent volumes and not for equal volumes, we obtain numbers, that appear to be in part equal to each other, and in part to stand in a simple relation. Schröder is of opinion that the equivalent volumes of simple bodies suffer expansions by heat which stand in simple relations to each other when the equivalent volumes themselves have also simple relations. The equivalent volume of platinum and palladium is for instance 57, the equivalent volume of lead 114, consequently exactly twice as large; the expansion of the equivalent volume of platinum and palladium from 0° to 100° is 0·162*, that of the equivalent volume of lead is 0·974, consequently $6 \times 0{\cdot}162$. The fact that expansions do not stand in the same relation as the equivalent volumes, gives rise to some doubt as to the validity of this law. (*Pogg. Ann.*, Bd. lii., s. 282, &c.)

The equivalent volume of water is 112·5; its expansion from 0° to 100° amounts to 0·045668; the expansion of the equivalent volume is therefore $= 5{\cdot}13$, that is, $32 \times 0{\cdot}16$; the expansion of steam from 0° to 100° amounts, as in the case of all gases, to 0·366, whence it follows, that the volume 112·5 of a gas expands by 41 from 0° to 100°. This amount is eight times the expansion of water ($8 \times 5{\cdot}125$) and 8×32 times of the expansion of platinum, measured for equivalent volumes. Schröder is of opinion that the expansions of bodies are comparable in all conditions of aggregation, provided their equivalent volumes stand in simple relation to each other.

In connection with this view, we may mention that of Persoz, according to which an equal volume of gas or a multiple of that volume can be obtained from an equal volume of simple and compound bodies in their transition from the fluid or solid to the gaseous condition, (by which he finds the hypothetical specific gravities of the gases of all bodies,) and that the hypothetical specific gravity of the

* We obtain this number by multiplying three times the linear expansion from 0° to 100° by the equivalent volume at 0°. The linear expansion of platinum from 0° to 100° = 0·000984, three times this number, the cubic expansion, = 0·002952; this multiplied by 57 gives the equivalent volume of platinum.

gas of a body thus obtained is to that of steam, as the specific gravity of that body is to that of water. But Gmelin, (in his *Handbuch*, 4te Aufl., s. 58 u. 74,) has shown that Persoz not only starts with purely arbitrary views, but even with such as might be proved to be false, and that he confirms his calculations in part with observations altogether incorrect. 1 vol. of solid iodine gives 437 vols. of vapour; 1 vol. of phosphorus 310 vols.; 1 vol. of arsenic 440 vols.; 1 vol. of sulphur 230 vols.; 1 vol. of mercury 1500 vols. of vapour, whence the untenability of Persoz's view is made apparent. At the time Schröder traced the condensation induced by the union of solid bodies to their constituents, and not, as he now does, to the aggregate, and when he assumed the equivalent volume of the oxygen to be 32 (see page 13,) and not 64 as he now does, he endeavoured likewise to explain the different specific heat with which oxygen and the elements generally enter into combination as occasioned by the different condensation of the elements in these compounds. (*Pogg. Annal.*, Bd. lii., s. 269, &c.) He declared, by way of further confirming this proposition, that, if the atom-volume of a body suffer condensation according to simple relations, the specific heat of this atom will likewise change according to simple fixed relations.

It is well known that oxygen is contained with the specific heat of 30 in the oxides R O, and many oxides $R_2 O_3$, and $R O_3$; in all these oxides the equivalent volumes of the oxygen amounts to 32, as shown by the first table, at page 14. The specific heat of the oxide of tin, $Sn O_2$ is 87; if we deduct the specific heat of Sn, that is, 40, there will remain 47 for the specific heat of O_2, consequently 23 for that of O, that is nearly $\frac{3}{4} \times 30$; oxygen is therefore contained in oxide of tin with $\frac{3}{4}$ of the specific heat, with which it is contained in the first-named oxides. According to the second table at page 14, oxygen occurs in the oxide of tin with the equivalent volume 16, that is, $\frac{1}{2} \times 32$; consequently with half as large an equivalent volume as the one, with which it appeared in the first-named oxides. According to Schröder, therefore, this condensation of volume to $\frac{1}{2}$ corresponds with the diminution of spe-

cific heat to $\frac{3}{4}$. The same holds good, according to his statement, for titanic acid, in which he likewise assumed the equivalent volume of the oxygen to be only 16, although it may safely be taken as 32.

The specific heat of iron pyrites : $Fe S_2$ is 97. If from this we deduct the specific heat of Fe, that is, 40, there will remain a specific heat of 57 for S_2, consequently the specific heat of 28 for S, whilst the specific heat of S in a free condition, is equal to that of iron, namely 40. The number 28 is again about $\frac{3}{4} \times 40$. The equivalent volume of iron pyrites is 147, if from this we deduct the original equivalent volume of the iron, 45, there will remain for S_2 the equivalent volume 102, and for S the equivalent volume 51, whilst in a free condition, for S, it amounts to 100. Thus, by the union of iron with sulphur to form iron pyrites, a condensation of $\frac{1}{2}$ the equivalent volume of the sulphur has taken place, and here again consequently a diminution of the specific heat to $\frac{3}{4}$ corresponds to this condensation of $\frac{1}{2}$.

As the equivalent volume of oxygen in $Mo O_3$ and $Wo O_3$ amounts to 64, that is 2×32, (see page 14, second table) it might be supposed that the specific heat of O in these combinations would be greater than 30; such, however, is not the case, it amounting only to 26. The specific heat of $Mo O_3$ and $Wo O_3$ is for instance 118, and if we deduct from this the specific heat of Mo and Wo, that is 40, there will remain for O_3 the specific heat 78, and consequently for O that of 26. It is also worthy of notice that oxygen is contained in oxide of iron with an equivalent volume of 32, and in oxide of chromium with the equivalent volume of 16; notwithstanding that the specific heat of both oxides is equally great.

The study of the equivalent volumes of bodies in a solid and liquid condition deserves not less attention than the study of the equivalent volumes of bodies in a gaseous state, and, indeed, the former possesses a peculiar interest from the relation in which the equivalent volume in a solid condition stands to isomorphism. It has occupied a large space in this essay from the few definite points that could be advanced upon the subject,

and the many different views that required to be enumerated. That the relation, in which the equivalent volume of a combination stands to the equivalent volume of its constituents should not be accurately known, cannot excite surprise, if we bear in mind that the data on which the establishment of these relations is based, are either wholly wanting, or are deficient, and, without doubt, in some cases, erroneously conceived. Thus exact details are wanting for most bodies with reference to the enlargement of volume (dilatation) suffered by the action of heat; the specific gravities are generally known only with some approximation to the truth, and the data obtained for the fusion and boiling points deserve, for the most part, still less confidence than those concerning the specific gravities. As it was impossible to find the law of equivalent weights until the older and frequently most incorrect numerical data of the per-centage composition of the combinations had been replaced by others that were more accurate, so it will likewise be impossible to find the law of the equivalent volumes until correct data are obtained respecting dilatation, the fusion and boiling point, and the specific gravity of bodies.

This would seem to be the most fitting place to say a few words upon Gmelin's atomic numbers. We have named equivalent volumes of bodies in a gaseous and liquid or solid condition, the relative volumes, which are filled by an equivalent of the bodies, in a gaseous, or liquid, or solid condition. In the comparison of the equivalent volumes in a gaseous condition the equivalent volume of oxygen has been set down as $=1$; the equivalent volume of hydrogen was therefore $=2$, that of the vapour of alcohol $=4$, &c.; in comparing the equivalent volumes in a solid and liquid condition, the quotients obtained by the division of the specific gravities by the equivalent weights have been directly made use of, since no such simple relation between the equivalent volume as observed in the gaseous condition has as yet been established. If now, in accordance with the atomic theory, we substitute the word *atom* for that of equivalent, we obtain the word atom-volume from the word equivalent volume, and if further we use the words atoms and atom-volume in the definition given for the

equivalent volumes of bodies, we shall have as follows: atom-volumes of bodies in a gaseous, liquid, or solid condition are the relative volumes occupied by an atom of the body in a gaseous, liquid, or solid condition. According to this definition, the volume of an atom of iodine in a state of vapour is 400 times greater than the volume of an atom of iodine in a solid condition, for 1 vol. of solid iodine yields above 400 vols. of vapour of iodine; 1 vol. of fluid mercury yields about 1500 vols. of vapour of mercury, the atom of mercury consequently in a gaseous state fills a space 1500 times greater than that which it occupies in a solid form.

The atoms of bodies are impenetrable, and not capable of expansion; they are not in immediate contact with each other, do not fill space uniformly, but are kept at a certain distance from each other, which changes with the density of the body. If we suppose 1500 atoms to be contained in a certain volume of fluid mercury, the distance of the atoms from one another will increase so much on their transition from the fluid to the gaseous form, that a volume of the vapour of mercury, equal to a volume of fluid mercury, will only contain one atom of the metal. We are very generally accustomed to say, that the atoms are surrounded by spheres of heat, which enlarge by heating, and on a transition from the solid to the gaseous condition, and diminish by cooling, and on a transition from the gaseous to the solid state*.

Gmelin considers it better, instead of giving the relative volumes taken up by an equal number of the atoms of bodies, conversely to give the number of the atoms contained in an equal volume of the bodies, and thus speaks of *atom-numbers*

* Löwig says, in his *Chemie der Organischen Verbindungen*, 1844, Bd. i., s. 91, "According to the atomic view, the individual atoms, of which a connected mass consists, cannot perfectly fill space; it is to be assumed that each individual atom consists of a solid part surrounded by a sphere of heat, standing in the same proportional relation to the individual atoms, in which the atoms combine together, so that the quantity of the casing of heat is equivalent to the quantity of the atomic weight. If the materiality of heat be admitted, then the atoms will combine with heat, according to definite proportions, in the same manner as these atoms combine together." It is, however, clear that heat cannot be anything material if we think of it as existing in the manner specified between the atoms of bodies; if it were anything material it would likewise consist of atoms, and what would then intervene between these atoms?

instead of atom-volumes. I do not consider that the least advantage to science is gained by this change. It will be evident in what relation the atom-number stands to the atom-volume, of which it forms, as one may say, the converse. The atom-volume shows the relative volumes of the atoms of bodies; if, therefore, we divide the number 1 by the atom-volumes, we must obtain the atom-numbers. The atom-volume is the quotient yielded by the division of the specific gravity by the atomic weight, and the atom-number is the quotient obtained by the division of the atomic weight by the specific gravity. Thus the more atoms of a substance are contained in a definite space, and the denser the atoms are, the greater must be the specific gravity; the specific gravity of a substance is, therefore, the product of the atom-number and the atom-weight.

If we assume that 1 equiv. of hydrogen, nitrogen, chlorine, &c., fill 1 vol., 1 equiv. of oxygen, phosphorus vapour, and vapour of arsenic will fill $\frac{1}{2}$ vol., and 1 equiv. of sulphur only $\frac{1}{6}$ vol. If, therefore, 1 vol. of hydrogen, &c., contain 1 at. of hydrogen, an equal volume of oxygen, that is, 1 vol. of oxygen must contain 2 at. of oxygen, and 1 vol. of vapour of sulphur contain 6 at. of sulphur. Thus Gmelin distinguishes between 1 atom-gases, (hydrogen, iodine, bromine, chlorine, nitrogen, mercury,) 2 atom-gases, (as phosphorus, arsenic, oxygen,) 6 atom-gases, (as sulphur,) and he maintains that in elastic fluid compounds there are besides $\frac{2}{3}$, $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$ atom-gases*. On a substance assuming a gaseous form, its atoms become surrounded by spheres of heat, whose volumes are as 1 (in the 6 atom-gases,) as 3, (in the 2 atom-gases,) as 6, (in the 1 atom-gases,) as 9, (in the $\frac{2}{3}$ atom-gases,) as 12 (in the $\frac{1}{2}$ atom-gases,) as 18, (in the $\frac{1}{3}$ atom-gases,) as 24, (in the $\frac{1}{4}$ atom-gases.)

If we set down the atom-volume of oxygen as $=1$ instead of that of hydrogen, we shall of course obtain other atom-numbers. Oxygen, phosphorus, arsenic, &c., will then be 1

* For making use of the expressions $\frac{1}{2}$ atom-gas, $\frac{1}{4}$ atom-gas, &c., we must ask the indulgence of the severe critic, as much as when we say that 1 atom of mercury in a gaseous form fills a space 1500 times greater than it occupies when in a liquid condition.

atom-gases, hydrogen, nitrogen, chlorine, &c., $\frac{1}{2}$ atom-gases, and sulphur a 3 atom-gas.

The atom-numbers 1, 2, 6, &c., for hydrogen, oxygen, and sulphur, are reduced numbers, expressive of the relation in which the atom-numbers resulting from the division of the specific gravity of the gas by the atom-number stand to each other. Gmelin has also calculated such reduced atom-numbers for the solid and liquid elements; and they may easily be deduced from the Table at page 4, which gives the atom-volumes of the elements. Potassium has the greatest equivalent and atom-volume, it must, therefore, have the smallest atom-number; and it is evident, that the elements whose atom-volume is equal, must also have equal atom-numbers.

II.

MEMOIR.

STUDIES ON THE CONNECTION EXISTING BETWEEN THE ATOMIC WEIGHTS, CRYSTALLINE FORM, AND DENSITY OF BODIES.

By M. Filhol.

Among the objects of research, that have most frequently attracted the attention of physicists and chemists, we may mention the study of the relation existing between the atomic weight, the density and the crystalline form of different bodies, whether simple or compound. The researches made in this department of science by Dumas, Boullay, Kupfer, Persoz, Schröder, Kopp, and Ammermüller, have made us acquainted with a series of results as remarkable as they were unexpected.

As the atomic weights, which have served to establish the remarkable approximations referred to in the memoirs of the authors alluded to, have, for the most part, been very considerably modified during the last few years, I have thought that it would not be wholly devoid of interest, to examine whether the laws established by these chemists were still valid, notwithstanding the changes that had been introduced; it has likewise appeared to me, that a critical *resumé* of all that has been published up to the present day, and a consideration of the new views developed in these works, might not be deemed wholly unimportant.

With these views, I purpose, in the present memoir,—

1st. To consider the researches of the different authors whom I have already cited, and to examine into the relations they have established between the atomic weight, the specific weight, and the crystalline form of bodies, in order to see whether they can be retained without alteration.

2nd. To discuss the value of the views developed by M. Kopp, relative to the manner in which we ought to consider the chemical constitution of salts.

3rd. And in conclusion, to unfold several of my own views on this subject.

I purpose devoting a separate and special memoir to the consideration of the relation existing between the specific volume of isomorphous, or homëomorphous bodies and their crystalline form. I will, however, before proceeding further, give the atomic weights and the densities on which my calculations have been based.

I have made choice amongst the different determinations of atomic weights of those which appeared to me to merit most confidence, without in any way being biassed by the greater or less support which any of the numbers might lend to the views I was desirous of developing. The numbers which I selected are as follows:—

ATOMIC WEIGHTS.

Barium	854·85	Magnesium	157·75
Cadmium	696·17	Manganese	344·44
Calcium	250·00	Mercury	1250·90
Carbon	75·00	Potassium	488·84
Chlorine	443·02	Silver	1349·01
Chromium	249·83	Sodium	287·17
Copper	396·00	Sulphur	200·00
Iodine	1585·57	Strontium	545·60
Iron	350·00	Tin	735·03
Lead	1294·50	Zinc	406·59

I have myself determined a great number of densities, of which I will give a table. My calculations have been made with the most careful attention.

Specific Gravities. *By* M. Filhol.

Iodic Acid		4·250
Arsenious „		3·884
Arsenic „		4·250
Protoxide of	Barium	5·456
	Strontium	4·611
	Calcium	3·180
	Zinc	5·612
	Lead	9·361
Binoxide of	Copper	6·322
Alumina		4·154
Anhydrous Chloride of	Potassium	1·994
	Sodium	2·240
	Barium	3·750
	Strontium	2·960
	Calcium	2·240
	Iron	2·528
Iodide of	Potassium	3·056
	Sodium	3·450
	Barium	4·917
	Lead	6·384
	Mercury (bin)	6·250
	Silver	5·500
Monosulphide of	Potassium	2·130
	Sodium	2·471
Carbonate of	Potash	2·267
	Soda	2·509
	Baryta	4·565
Anhydrous Sulphate of	Potash	2·625
	Soda	2·629
	Strontia	3·770
	Lime	3·102
	Magnesia	2·628
	Zinc	3·400
	Copper	3·530
	Iron	2·841
Anhydrous Sulphate of	Silver	5·410
	Lead	6·300
Nitrate of	Soda	2·260
	Baryta	3·200
	Strontia	2·857
	Lime	2·240
	Lead	4·581
Hydrate of	Potash	2·044
	Soda	2·130
	Baryta (Ba O, H O)	4·495
	Strontia (Sr O, H O)	3·625
	Baryta (Ba O, 9H O)	1·656
	Strontia (Sr O, 9H O)	1·396
	Zinc	3·053
	Lime	2·078
Crystallized Chloride of	Barium (Ba Cl + 2H O)	2·664
	Strontium	1·603
	Calcium	1·635
	Magnesium	1·558
	Iron	1·926
Crystallized Sulphate of	Soda	1·520
	Lime	2·331
	Magnesia	1·751
	Alumina	1·569
	Iron	1·904
	Zinc	2·036
	Copper	2·286
Crystallized Nitrate of	Strontia	2·113
	Lime	1·780
Anhydrous Borax		2·367
Crystallized Borax		1·692

Amongst these densities there are a great number which agree with those determined by Boullay, Mohs, Karsten, &c., others, on the contrary, differ very widely from them; as, for instance, those of baryta and strontia, but I have so frequently, and always with the greatest care, repeated the process of weighing these two oxides, that I believe I may affirm that the error is not on my side.

I will now proceed to examine the works of each of the authors to whom I referred at the beginning of this Memoir, taking them in the order in which they were published.

Kupfer published in 1824 (*Annales de Chimie et de Physique*, 2me Série, tome xxv., page 337,) a Memoir in which he gave the exposition of a method, by which, according to his views, the density of a large number of bodies may be determined.

Suppose p and p' to be the atomic weights of two different substances, s and s' their densities, and y and y' the volumes of their primitive form, the semi-axis being assumed to be equal to unity; then we have $\frac{p\,s}{y} = \frac{p'\,s'}{y'}$.

In order to obtain exact results by this formula, it is necessary that the two substances to be examined should belong to the same system of crystallization.

Kupfer admits only four primitive forms, viz.; the regular octohedron, the octohedron with a square base, the octohedron with a rhombic base, and the rhombohedron.

Kupfer's memoir contains the calculations of a very large number of densities, all of which agree in a most remarkable manner with the results yielded by experiment; and this agreement is much the more extraordinary as there are serious grounds, amounting almost to positive evidence, for believing that the relation indicated by Kupfer cannot be true.

Suppose, for instance, that in the equation $\frac{p\,s}{y} = \frac{p'\,s'}{y'}$, y becomes equal to y'*, we shall have $p\,s = p'\,s'$, that is to say, the densities will be inversely as the atomic weights: which is by no means in conformity with experience. On examining with particular attention the memoir of which I

* Many examples of this may be found in Kupfer's Memoir.

speak, we shall soon detect the cause of this surprising agreement, which results from Kupfer multiplying or dividing the atomic weights of either of the two bodies under examination sometimes by whole numbers, and sometimes by fractions, and by this means always concludes in satisfying the conditions of the problem. Thus the atomic weight of phosphate of lime is multiplied by $\frac{3}{8}$, that of the emerald by $\frac{1}{4}$, that of amphigene by $\frac{1}{3}$, and that of Siberian idocrase by $\frac{3}{2}$, &c. The necessity of thus having recourse, in a great number of cases, to the multiplication of atomic weights by numbers chosen in so arbitrary a manner, affords reason to doubt the exactness of the preceding formula; and I am about to show that other considerations lead to the proof that it is not accurate.

Dumas discovered long since a simple relation existing between the atomic and the specific weights of a large number of bodies; and this relation is moreover connected with the crystalline form, as it only exists in isomorphous bodies. If p be the atomic weight of a body, d its density, v its atomic volume, we shall have $v = \frac{p}{d}$.

Dumas was the first to demonstrate that the value of v was sensibly the same for all bodies, whose isomorphism had been established by Mitscherlich; and far from shaking the validity of this law, the changes that have subsequently been made in several atomic weights have contributed to prove its accuracy. We shall shortly see that Kopp has proved its applicability to compound, no less than to simple bodies.

Thus, then, for perfectly isomorphous bodies $\frac{p}{d} = \frac{p'}{d'}$, or what is the same, $p\,d' = p'\,d$. Consequently Kupfer's formula, which supposes $p\,d = p'\,d'$, is necessarily false.

The study of the relations existing between the atomic weight, the density, and the crystalline form of compound bodies, is rendered very difficult, owing to the combination of bodies being almost always accompanied by a considerable change of volume, and that it is very rare for the volume of a compound to be represented by the sum of the volumes of its components. We may, therefore, easily conceive that the

density of a compound cannot be determined by calculation until the law regulating the change of volume experienced by the body in the act of combination shall be accurately known. Several chemists have endeavoured to discover it, and I will give a rapid analysis of their labours.

The first memoir written on this subject is by Boullay. After having arranged in one table the actual density of a large number of compound bodies, this chemist compares their density to that which would be possessed by these bodies, if their elements had combined without experiencing any change of volume; he then proceeds to demonstrate that several cases may present themselves whilst the bodies are combining.

1. The density of the compound may be the same as that of the components.

2. It may be different.

On comparing the actual density of several sulphides with their calculated density, he then finds that in this class of compounds, the combination is always effected with condensation; the inverse holds good for iodides. Here the volume of the combination is greater than that of the components. We must, however, according to Boullay, except iodide of potassium, (and I would also add to this the iodides of sodium and barium).

M. Boullay finally examines if the condensation is the same for those bodies which yield the same formula of atomic composition, and here he can discover no analogy.

The memoir that I have been considering is essentially characterised by the absence of all preconceived views, the experiments having invariably been made upon compounds whose elements were known in their solid state. M. Boullay appears to have adopted the best means of discovering the laws of condensation or of dilatation, but I will subsequently show, that in making choice of other compounds, and proceeding in other respects in the same manner as M. Boullay, we arrive at curious approximations, that he had not observed. It must not be forgotten that sulphur, which presents so many anomalies in its physical properties, may occur in different states in certain sulphurets, and this fact probably explains the reason

why M. Boullay did not observe any relation between their co-efficients of condensation.

Next in point of date to the memoir I have been considering, succeed the researches of M. Persoz.

Without entering into any unnecessary detail, I would call attention to the fact that M. Persoz calculates *à priori* the density of bodies in the following manner: he supposes that 1 equiv. of oxygen weighing 100 grammes, and occupying a volume of 70 liters, 1 equiv. of any other body will, if reduced to vapour occupy a space either of 70 liters, or 70 multiplied by 2, 4, 8, 16, 32—or by 3, 6, 12, 24; this being assumed, he seeks the hypothetical weight of 1 liter of the vapour of the body whose density he wishes to determine, and then establishes the following relation:

0·8003	:	P	: :	1	:	x
Weight of 1 liter of aqueous vapour.		Weight of 1 liter of the vapour of the body.		Density of the water.		Density sought.

M. Persoz presents in support of his views, a table in which the density of several bodies is expressed with a surprisingly close approximation to the results yielded by experiment. But as soon as we attempt to apply his method in a general manner, we meet with so many exceptions as to render it impossible to admit the validity of the proposed law: I will only instance a very small number of cases; many similar ones might, however, be found.

	Calculated Density.	Observed Density.
Iron	6·24	7·73
Tin	6·55	7·28
Copper	7·16	8·90
Silver	12·03	10·47
Manganese	6·00	8·00
Arsenic	8·35	5·96
Sulphur	1·78	1·99

M. Baudrimont states the relation indicated by M. Persoz differently: according to him the molecular and specific weights of bodies of a determined nature are certain multiples or submultiples of one another, and these relations are the same for isodynamic bodies. We may, therefore, conclude that isodynamic bodies sensibly occupy the same volume with

weights proportionate to their molecules. To demonstrate this law, M. Baudrimont compares the equivalents of bodies and their density to the same unit. The unit he takes is 56·24, the half of the number representing the equivalent of water; by dividing the chemical equivalents of bodies by the semi-equivalent of water, he obtains numbers that bear a simple relation to the densities. The following table will give some idea of this.

Bodies.	Atomic Weight.	$\frac{HO}{2}=1$.	Density observed.	Relation.
Diamond	1504·5	2·66	3·55	2 : 3
Chrome	349·83	6·21	5·90	
Manganese	344·14	6·12	8·02	
Iron	350·00	6·22	7·778	
Zinc	406·59	7·22	7·21	
Nickel	369·14	6·38	8·41	
Cobalt	368·99	6·65	8·53	
Copper	396·00	7·03	8·89	1 : 1
Silver	674·5	11·99	10·47	
Palladium	665·9	11·84	11·80	
Platinum	1333·5	21·93	21·60	
Gold	1228·31	21·83	19·25	
Tungsten	1183·00	21·03	17·60	
Cadmium	696·77	12·38	8·60	
Arsenic	468·24	8·32	5·96	3 : 2
Molybdenum	598·52	10·62	7·40	
Lead	1294·5	23·01	11·35	
Antimony	806·45	14·34	6·70	
Tin	735·30	13·07	7·29	2 : 1
Selenium	494·58	8·79	4·30	
Phosphorus	196·4	3·49	1·77	
Iodine	792·5	14·08	4·94	3 : 1
Bromine	499·8	8·88	3·187	
Sodium	287·17	5·10	0·97	5 : 1
Potassium	489·94	8·71	0·86	10 : 1

The relations indicated in this table are by no means rigorous, and very considerable errors must have been made in the determination both of the atomic weights and the densities before such results could have been obtained. I have endeavoured to discover the changes that must necessarily be made in the densities in order to arrive with exactitude at these relations, and the following table gives the result of my calculations.

Bodies.	Density obtained.	Density calculated.	Bodies.	Density obtained.	Density calculated.
Diamond	3·55	3·99	Cadmium	8·60	8·25
Chrome	5·90	6·21	Arsenic	5·96	5·54
Manganese	8·02	6·12	Molybdenum....	7·40	6·74
Iron	7·778	6·22	Lead	11·35	11·50
Zinc	7·21	7·22	Antimony	6·70	7·17
Nickel	8·41	6·38	Tin	7·29	6·53
Cobalt	8·53	6·55	Selenium	4·30	4·39
Copper	8·89	7·03	Phosphorus	1·77	1·74
Silver	10·47	11·99	Iodine	4·94	4·69
Palladium	11·80	11·84	Bromine....	3·187	2·96
Platinum	21·60	21·93	Sodium	0·97	1·02
Gold	19·25	21·83	Potassium	0·86	0·871
Tungsten	17·60	21·03			

The difference existing between the density calculated and the density observed for carbon, manganese, iron, nickel, cobalt, copper, silver, gold, and tin, is too great to be attributed to errors of observation. M. Baudrimont, moreover, states that this simple relation is not observed for sulphur, mercury, and bismuth, consequently out of 28 bodies we find 12 which yield numbers widely remote from the relation indicated in the preceding table.

A law which admits of such numerous exceptions, and supposes so many errors in its general results, cannot, in my opinion, be received. Moreover, M. Baudrimont himself admits that these numbers are merely approximative, and that in wishing to submit them to a general law we may deviate from the truth by the corrections we attempt to make. Here it must be observed, and I think not unjustly, that in order to obtain strictly accurate results, we ought to be able to take some account of the comparative specific heat in different bodies, of their molecular condition, and, above all, of their conditions of polymorphism.

M. Kopp has published a series of very important memoirs on specific volumes; he first attempted to determine by calculation the density of several bodies whose determination had not been made by experiment, and presented great difficulties; as barium, strontium, calcium, and magnesium. It is a very singular fact, that he arrived at different numbers for the

density of these metals, according as to whether he calculated according to that of the protoxide or that of the sulphate. Thus—

The density of Barium deduced from	....	.... $BaO = 3{\cdot}60$
„	„	.... $SO_3\,BaO = 5{\cdot}50$

M. Kopp takes the number 4·55, the mean of the two preceding numbers. He likewise finds—

The density of Strontium deduced from	....	.... $SrO = 2{\cdot}37$
„	„	.... $SO_3\,SrO = 3{\cdot}35$

and he adopts the mean number 2·86.

In introducing into the calculations established in his memoir the specific volumes of barium and strontium, deduced from the preceding densities, M. Kopp arrives at results, which do not accord with those yielded by experiment, and he thence concludes that barium and strontium do not combine with their primitive specific volume, but with the following volume.

Barium	$v = 143$
Strontium....	$v = 108$

I have already remarked that the numbers given by Karsten as representing the density of baryta and strontia were incorrect; consequently the results obtained by Kopp in calculating from them the preceding densities must likewise be false.

M. Kopp does not explain in his memoir how he was led to represent the specific volumes of barium and strontium by the numbers 143 and 108, but they agree so well with the results yielded by experiment in all the tables he has calculated, that we may reasonably consider them to be exact; and I will proceed to demonstrate that they are so.

In accordance with M. Kopp's views, we shall find all the facts established, if we admit that all metals excepting potassium, sodium, barium, strontium, magnesium, calcium, and aluminum enter into combination with a change of volume. Those that I am about to cite combine with the volumes specified, which differ considerably from their actual volume.

	Actual Volume.	Volume in the Combination.
Potassium	583	234
Sodium	291	130
Barium	188	143
Strontium	191	108
Calcium	156	60
Magnesium	156	40

I have found, in opposition to the views entertained by M. Kopp, that barium and strontium are comprehended in the class of metals which may be considered to retain their primitive volume in combinations; it must be understood that in making these calculations I have taken the data furnished, as I suppose correctly, in M. Kopp's memoir. On referring to the tables in his memoir (*Annales de Chimie et de Physique*, 3me série, tome iv., p. 462), it will be seen that the facts can be perfectly well received, on the supposition that the volume of oxygen contained in the oxides is equal to 16, 32, or 64.

If we assume this law to be correct, and seek the density of barium and strontium according to the densities that I have already given for baryta and strontia, we shall have:—

	Actual Specific Volume.	Volume of the Metal.
Ba O	175	175 − 32 = 143
Sr O	140	140 − 32 = 108

Thus, the numbers 143 and 108, which M. Kopp derived from experiment, are deduced by calculation from the densities of baryta and strontian, as given above.

It must necessarily be admitted, that the other metals, as potassium, &c., actually enter into combination with a volume different from their actual volume.

I will not at present pause to consider the views developed by M. Kopp with regard to the relations existing between the crystalline form and the specific volume, as my object is to enter fully into the subject in a special memoir, which I purpose at a subsequent period to lay before the Academy. I will now only direct my attention to an enquiry into the correctness of M. Kopp's opinions relatively to the manner in which we ought to consider the constitution of salts, and examine how far his views on the subject are supported by the study of specific volumes.

All the arguments advanced by M. Kopp are based upon a very curious observation made by M. Schröder, which I must explain before I proceed further.

M. Schröder observed that when, after having calculated the specific volume of a series of analogous combinations (oxides, chlorides, sulphates), he deduced from the volume of each of the combinations the volume of the corresponding constituents, the same number was often obtained to express the volume of the common constituents. (See *Annales de Chimie et de Physique*, 3me série, tome iv., p. 474.)

Thus, on subtracting from the specific volume of nitrates the volume of the metals entering into their composition, we always obtain as the remainder the number 358, which expresses the specific volume of NO_6, in the same manner as for carbonates, the volume of $CO_3 = 151$, &c.

We will now examine the consequences deduced by M. Kopp from his calculations. Two theories present themselves in explanation of the chemical constitution of salts. According to the first and more ancient one, a salt produced by the combination of an oxacid with a metallic oxide must be considered to include each of the two elements that have entered into its formation: thus, sulphate of potash equals $SO_3\,KO$. According to the second theory, the oxygen of the oxide forms with the acid a new compound, which will combine with the metal: thus, sulphate of potash would be $SO_4\,K$.

Many arguments may be advanced for and against each of these theories, I will, however, limit my remarks to the discussion of the support which, according to M. Kopp, is derived by the second of these theories from a study of specific volumes.

We will then consider, as this chemist proposes, both the specific volumes of the salts, formed by an oxygen acid, and those of the best known metals, as for instance the nitrates of lead and silver.

We obtain by experiment for the specific volume of nitrate of silver, $v = 488$; for that of nitrate of lead, $v = 472$; for the specific volume of silver, $v = 130$; for that of lead, $v = 114$; for the specific volume of oxide of silver, $v = 194$; for that of oxide of lead, $v = 146$.

What theory can need more hypothesis to express the volume of the salts in question? The theory of hydracids, supposing the metal to be contained as such in these salts, determines the volume of $N O_6$:

$Ag N O_6$	=	488	$Pb N O_6$	=	472
Ag	=	130	Pb	=	114
$N O_6$	=	358	$N O_6$	=	358

The specific volume of $N O_6$ is thus of the same value in both cases; here only one supposition is required to express the density of these salts, and the specific volume of $N O_6$ is established in both cases as being equal to 358.

The theory of oxygen acids does not admit of similar simplicity; it supposes the metal contained in the salts to be in the condition of an oxide, and in order by this means to determine the specific volume of $S O_3$, we have—

$Ag O N O_5$	=	488	$Pb O N O_5$	=	472
$Ag_2 O$	=	194	Pb O	=	146
$N O_5$	=	294	$N O_5$	=	326

The theory of oxygen acids thus yields a different remainder for the volume of $N O_5$ in the different salts; consequently the theory of hydracids is necessarily simpler than the former with regard to the explanation of density, and considered from this point of view has the greater appearance of probability.

These arguments are plausible, but a very little consideration will be sufficient to show that they are much less valuable than we might at first sight be inclined to believe. And all the preceding reasons are actually based upon an incorrect density (that of the nitrate or the oxide of silver), or upon an exception, as I am about to show. If we suppose for instance, that the theory of oxygenous acids be correct, and proceed with regard to other salts as we have done with the nitrates of silver and of lead, we shall have:

$N O_5 Ba O$	=	501	$N O_5 Sr O$	=	466
Ba O	=	175	Sr O	=	140
$N O_5$	=	326	$N O_5$	=	326

On examining other classes of salts;

		Vol.			Vol.
Sulphate of Zinc	$S O_3$ Zn O =	294	Sulphate of Copper	$S O_3$ Cu O =	280
	Zn O =	90		Cu O =	76
	$S O_3$ =	204		$S O_3$ =	204
Carbonate of Baryta	$C O_2$ Ba O =	294	Carbonate of Zinc	$C O_2$ Zn O =	209
	Ba O =	175		Zn O =	90
	$C O_2$ =	119		$C O_2$ =	119

The following tables will serve to prove that the examples I have cited have not been arbitrarily chosen, but that all the salts comprised in M. Kopp's tables, (excepting the salts of silver,) lead to the same result. I believe I ought to remark, that if we suppose an error to have been made in the determination of the density of oxide of silver, the salts of this metal would be comprehended under the general law. An error of this nature seems not improbable, for the numbers given by different authors for the density of oxide of silver vary very considerably from one another, as we may see by the following statements:—

Density of oxide of silver	7·14	according to	Herapath.
„ „	7·25	„	Boullay.
„ „	8·26	„	Karsten.

However this may be, I am about to show that the theory of oxygen acids leads to results which are quite as satisfactory as those obtained by the theory of hydracids. (I would remark here that the following calculations are all based upon the densities and chemical equivalents adopted by M. Kopp.)

Sulphates. The theory of hydracids furnishes a good explanation of facts, if we suppose that the compound $S O_4$ experiences two modes of condensation in its combinations. Thus, in certain sulphates, its volume equals 186, whilst in others it is equal to 236.

The theory of oxygen acids likewise accords well with the facts observed, if we admit that the compound $S O_3$ experiences two modes of condensation, and that its specific volume equals 154 in some sulphates, and 204 in others.

SULPHATES. $SO_3 = 154$; $O = 32$. (First Series.)

Sulphates of	Chemical Equivalent.	Density of the Salt.	Specific Volume of the Salt.	Specific Volume of the Metal.	Specific Volume of Oxygen.	Spec. Vol. of the combined Oxide.	Spec. Vol. of Sulphuric Acid.	Calculated Volume of the Salt.
Lead	1895	6·32	300	114	32	146	154	300
Baryta	1458	4·43	329	143	32	175	154	329
Potash ...	1091	2·60	420	234	32	266	154	420
Strontia	1148	3·90	294	108	32	140	154	294

$SO_3 = 204$; $O = 32$. (Second Series.)

Copper	997	5·34	280	44	32	76	204	280
Zinc	1004	3·42	294	58	32	90	204	294
Lime	857	2·90	296	60	32	92	204	296
Magnesia	759	2·75	276	40	32	72	204	276
Soda	892	2·44	366	130	32	162	204	366

CHROMATES. The density of Chromates may be well expressed by assuming the number 196 as the specific volume of Chromic Acid.

Chromates of	Chemical Equivalent.	Density of the Salt.	Specific Volume of the Salt.	Specific Volume of the Metal.	Specific Volume of Oxygen.	Spec. Vol. of the combined Oxide.	Spec. Vol. of Chromic Acid.	Calculated Volume of the Salt.
Lead	2046	5·98	342	114	32	146	196	342
Potash	1241	2·69	462	234	32	266	196	462

TUNGSTATES. Volume of the acid = 212; volume of oxygen = 32.

Tungstates of	Chemical Equivalent.	Density of the Salt.	Specific Volume of the Salt.	Specific Volume of the Metal.	Specific Volume of Oxygen.	Spec. Vol. of the combined Oxide.	Spec. Vol. of Tungstic Acid.	Calculated Volume of the Salt.
Lead	2877	8·04	358	114	32	146	212	358
Lime	1839	6·05	304	60	32	92	212	304

NITRATES. $O = 32$; $NO_5 = 326$.

Nitrates of	Chemical Equivalent.	Density of the Salt.	Specific Volume of the Salt.	Specific Volume of the Metal.	Specific Volume of Oxygen.	Spec. Vol. of the combined Oxide.	Spec. Vol. of Nitric Acid.	Calculated Volume of the Salt.
Lead	2071	4·40	472	114	32	146	326	472
Ammonia	1004	1·74	576	218	32	250	326	576
Baryta	1634	3·20	501	143	32	175	326	501
Potash	1267	2·14	592	234	32	266	326	592
Soda	1063	2·19	488	130	32	162	326	488
Strontia	1324	2·84	466	108	32	140	326	466

CARBONATES. $O = 32$; $CO_2 = 119$.

Carbonates of	Chemical Equivalent.	Density of the Salt.	Specific Volume of the Salt.	Specific Volume of the Metal.	Specific Volume of Oxygen.	Spec. Vol. of the combined Oxide.	Spec. Vol. of Carbonic Acid.	Calculated Volume of the Salt.
Cadmium	1073	4·63	232	81	32	113	119	232
Iron	715	3·67	195	44	32	76	119	195
Manganese	722	3·70	195	44	32	76	119	195
Lead	1670	6·30	265	144	32	146	119	265
Zinc	779	3·73	209	58	32	90	119	209
Baryta	1233	4·19	294	143	32	175	119	294
Lime	632	3·00	201	60	32	92	119	201
Magnesia	534	2·80	191	40	32	72	119	191
Potash	866	2·25	385	234	32	250	119	385
Soda	667	2·37	281	130	32	162	119	281
Strontia	923	3·56	259	108	32	140	119	259
Lime .... } Magnesia }	1166	2·90	402	{ 60 { 40	32 32	92 72	119 119 }	402

The preceding calculations will, if I am not deceived, show that no arguments can be drawn from the study of specific volumes either for or against the theories in question, and that the latter remain precisely the same as they were before these observations were made.

To the labours of M. Kopp succeed those of Ammermüller, who has established a law whose expression, modified by Poggendorf, is as follows:

The specific weights of the combinations of a radical with an electro-negative body are to one another as the corresponding atomic weights, either directly, or after multiplying them by certain simple fractions.

This law is verified in a great many cases, but an objection may be advanced against it which I think of the greatest importance. Thus, if we examine the tables drawn up by M. Ammermüller, we shall not fail to perceive that the fractions by which he multiplies the atomic weights are very far from being simple fractions, and this is so fully the case that by pursuing his method of working out the calculation we are always certain of arriving at a result in conformity with the one required by the experiments, and that even when we have started from results, which are evidently false. This may be proved by M. Ammermüller's own calculations. He calculates the density of binoxide of lead from that of the protoxide, supposed to be 8·01, and he thus arrives by calculation at a fairly correct determination of this density. But the real density of protoxide of lead is, at the least, 9·3; M. Ammermüller has, therefore, arrived at accurate results, although the data on which his calculations were based are evidently incorrect. This instance will, I think, be sufficient to show that this law cannot be regarded as valid.

The last author whose work I would consider is M. Schröder, and the conclusions he arrives at are to this effect:—

1. That the specific volume of a body may be equal to the sum of the volumes of its elements. (This proposition is based upon the observations made by M. Boullay.)

2. That any element may occur in different combinations under different conditions, in such a manner that its specific volume varies in the same relation as the numbers 1, 2, 3, 4, 5, 6, &c. This law comprehends that of condensation.

3. That the condensation of any one of the elements of a compound body may vary according to the same relation of the combination. (This fact forms the basis of isomerism.)

The fourth law relating to isomorphism agrees with that of M. Dumas, of which I have already spoken.

The truth of the first law is evident, and cannot be contested.

The second law does not appear to be sufficiently demonstrated: it may, however, be supported by numerous examples. Thus, we have already seen that the condensation of oxygen in the oxides or in the oxysalts is such that all the facts may be explained if we assume the volume of the oxygen to be

equal to 8, or to a multiple of 8. M. Kopp has shown that the condensation of chlorine in the chlorides is such, that the vol. of the chlorine is 196 for some, and 245 for others. Now these numbers, 196 and 245, are to each other as 4 to 5; but even here the law is often at fault. Whether, therefore, in the series of the sulphates, we adopt the views of Kopp, or those which I have developed, the numbers that express the atomic volume of $S O_3$, or of $S O_4$, in the two cases of condensation, are not exact multiples of one another.

I am now about to show, that if we study the changes of volume which occur during combination, setting aside all preconceived views, and without seeking to ascertain if the dilatation or the condensation have effected either of the components (which it seems to me to be very difficult to appreciate), we arrive at results that are not wholly unimportant.

Let us take the series of the chlorides, and let—

P represent the atomic weight of the chlorine.

D „ its density.

P' „ the atomic weight of the metal.

D' „ the density.

Δ „ the density of the chloride.

If we suppose that the elements have combined without a change of volume we shall evidently have:

$$\Delta = \frac{P + P' (dd')}{Pd' + P'd}.$$

If D represent the density of the chloride, as yielded by experiment, we shall always find $D > \Delta$, and $\frac{D - \Delta}{D}$ will express the co-efficient of condensation.

Let us take for the density of the chlorine the number 1·35. Faraday has found 1·33, Kopp admits 1·38.

Chlorides of	Density observed.	Density calculated.	Co-efficient of Contraction.
Potassium	1·994	1·039	0·478
Sodium	2·240	1·169	0·477
Barium	3·75	2·825	0·265
Strontium	2·960	2·266	0·234
Calcium	2·240	1·702	0·240
Lead	5·541	3·928	0·291
Silver....	5·530	3·920	0·291

Let us similarly examine the sulphates.

Sulphates of	Density calculated.	Density observed.	Co-efficient of Contraction.
Magnesia	2·266	2·628	0·137
Zinc	2·920	3·400	0·140
Copper	2·991	3·530	0·152
Baryta	3·393	4·440	0·236
Strontia	2·901	3·77	0·230
Lime	2·366	3·102	0·245
Lead	4·729	6·300	0·249

Supposing the density of $C O_2$ to be 0·83, we obtain the following results on applying this calculation to carbonates.

Carbonates of	Density calculated.	Density observed.	Co-efficient of Contraction.
Baryta	2·566	4·565	0·437
Strontia	1·949	3·610	0·460
Lime	1·415	2·720	0·477
Lead	3·491	6·470	0·459
Cadmium	2·783	4·455	0 380
Magnesia	1·293	2·966	0·563
Manganese	1·264	3·691	0·657
Zinc	1·860	4·445	0·581

Let us now proceed to consider from the same point of view, the hydrated and crystallized salts.

Hydrates of	Density calculated.	Density observed.	Co-efficient of Contraction.
Baryta ($Ba O + H O$)	3·718	4·495	0·172
Strontia ($Sr O + H O$)	2·989	3·625	0·175
Lime ($Ca O + H O$)	2·292	2·078	0·093
Magnesia (brucite)	2·336	1·920	0·178
Alumina (gypsite)	2·400	1·989	0·171
Alumina ($Al_2 O_3 + 8H O$)	1·786	1·459	0·183
Zinc ($Zn O + H O$)	3·434	3·053	0·110
Baryta ($Ba O + 9H O$)	2·288	1·656	0·276
Strontia ($Sr O + 9H O$)	1·911	1·396	0·269

Crystallized Sulphates of	Density observed.	Density calculated.	Co-efficient of Contraction.
Soda	1·520	1·375	0·093
Magnesia	1·751	1·434	0·180
Lime	2·331	2·099	0·099
Zinc	2·036	1·658	0·171
Iron	1·904	1·546	0·188
Copper	2·286	1·829	0·199

Crystallized Chlorides of	Density observed	Density calculated.	Co-efficient of Contraction.
Strontium	1·920	1·603	0·165
Barium	3·160	2·640	0·166

These tables evidently show that in a very large number of cases, setting aside all hypothesis, we find that the co-efficient of the condensation of the components that are most analogous to one another is the same in a chemical point of view.

These approximations further show that in a certain number of cases, the relation existing between the densities calculated for certain components of the same class is identical with that which exists between the densities yielded by experiment; and hence arises the possibility of calculating, *à priori*, the density of certain salts from that of their elements and that of a salt of the same species, having a great analogy with the one, whose specific weight we wish to determine. In fact we have $\Delta : \Delta' :: D : D'$.

I will give a few examples of this fact:—

Chloride of sodium .... $\Delta = 1{\cdot}169$, $D = 2{\cdot}24$
„ potassium.... .... $\Delta' = 1{\cdot}039$,
1·169 : 1·039 :: 2·24 : 1·990.

The density of chloride of potassium is given, by experiment, in the following numbers, 1·94; according to Kopp 1·92; to Karsten 1·994.

Sulphate of baryta .... $\Delta = 3{\cdot}393$, $D = 4{\cdot}440$
„ strontia .... $\Delta' = 2{\cdot}901$,
3·393 : 2·901 :: 4·44 : 3·796.

Experiment gives for sulphate of strontia 3·95; according to Breithaupt 3·59; to Karsten 3·77.

It will easily be seen that these instances might be greatly multiplied. Unfortunately, the relation which I have indicated is not absolutely general, and cannot be considered to constitute a law. It would have been easy to obtain identical numbers for the expression of the co-efficient of condensation of a large number of compounds by merely altering slight quantities in the densities used in my calculations, but I have left the numerous discrepancies that will be observed, in preference to altering any of the results yielded by experiment.

I would remark, in resuming the subject under discussion, that the study of the relations which I have considered is far from being so much advanced as may be supposed; it is easy, by modifying a few of the numbers serving to establish the calculations made on the subject, to obtain very promising approximations, but their perfect agreement with the results of experiments should excite some distrust, for it is extremely difficult in cases where we are unable to take account of numerous causes of error, to arrive at results which are as exact as the greater number of those given in some of the works I have analysed.

I am, however, far from wishing to depreciate the merit of those memoirs, and I trust that the authors will be convinced that nothing but a desire of throwing some degree of light upon a difficult subject, in which almost everything remains to be done, would have led me so unsparingly to expose the weak side of their several theories. The best means of arriving at truth is, in my opinion, to abstain as much as possible from all hypothesis; to endeavour above all to determine with great exactness the densities which form the basis of the calculations, and to make a comparison, whenever it is possible, between regularly crystallized bodies, since form has a great influence on density. Setting aside the equality of volume in isomorphous bodies, the views I have discussed in this memoir, whatever be the ingenuity with which they may be advanced, all admit of being contested.

I have endeavoured in the most impartial manner to show whatever was defective or good in each one. There are some

which certainly ought to be rejected, and others which must be very considerably modified before they can be brought into harmony with the results yielded by experiment, and others again which, although correct in a very great number of cases, are not so in all; these, it appears to me, ought not, however, to be over-hastily rejected, since a more careful study may show that they are capable of being made to accord in every case with experiment.

III.

REPORT.

ON THE LAWS, ACCORDING TO WHICH THE MIXING OF FLUIDS AND THEIR PENETRATION INTO PERMEABLE SUBSTANCES OCCURS, WITH SPECIAL REFERENCE TO THE PROCESSES IN THE HUMAN AND ANIMAL ORGANISM.

By Julius Vogel.

The phenomena, which we are accustomed to embrace under one general conception of animal life, are composed of an infinite number of individual processes, which stand in the most varied combinations and mutually reacting relations to each other. To these belong those mixtures of different fluids either in immediate and direct contact with each other, or separated by organic partitions (animal membranes), through which they pass and mix together. Many of these mixtures are so simple, and are so entirely identical with those processes, which every one in ordinary life has constant opportunities of observing, that they must be considered as scarcely deserving any further consideration; others, on the contrary, present many peculiarities, appearing at first to be highly paradoxical, and even in direct opposition to the laws of hydrostatics. Among these are the processes termed *Endosmosis* and *Exosmosis*, in which two fluids, that mix by means of a partition, so completely change their volumes, that the one fluid increases while the other, in a corresponding manner, diminishes. Cases of this nature have met with special and careful observation, and attempts of different kinds have been made to explain

the phenomena occurring in this process. The deeper, however, that we penetrate into these apparently paradoxical phenomena, the more does the mysterious obscurity that enshrouded them disappear; and the conviction forces itself upon the observer, that they are connected in the most natural manner with those simple cases, which give rise to no surprise, from our being familiarised to them by daily experience. A satisfactory explanation of the whole must, however, indispensably be preceded by an endeavour, starting from the simplest cases, to bring all phenomena occurring in the mixing of fluids under common laws. But these, like all other natural laws, cannot be established *à priori*, but must be obtained from the experience gained by experiments, which again presuppose observations. The conditions that may occur in the mixture of fluids are very numerous, and consequently the field opened to us is extensive, and the toil required most arduous. To this must be added, that it is not sufficient here to ascertain the influence of the general conditions at work, but that it must be considered rather the special task of science accurately to determine the *amount* of influence exercised in each individual case; that is, to establish it numerically. Such an exact mathematical mode of treating the subject is not only possible, but appears to be necessary, and simply in accordance with the requirements of science; it is, however, attended by difficulty, and presupposes an extended series of careful investigations, since each experiment of the kind, as the following considerations will show, necessarily presents many sources of error; it is only, therefore, such numerical results as have been derived from a large number of observations that can be received as approximating to a standard of correctness. The problem is one which can only be satisfactorily solved by degrees, and rather by the combined labours of many than by the researches of any single enquirer.

These and similar considerations have induced me to lay the following remarks before the public. Although I have deemed it best for the present to withhold the special data derived from a series of experiments (some of which were attended with much labour,) as they are insufficient for the establishment of a mathematical basis of this subject, and my object is

principally to draw attention to the leading phenomena which occur in the mixing of fluids, and in their permeation through organised substances, and, above all, to point out the mutual connection existing between these phenomena, I shall rejoice if these remarks should lead others to turn their attention to an enquiry which is of so much importance to physiology, and if the veil may thus be gradually removed, which now rests upon this subject, as well as upon many of the most important vital processes*.

1.

If two fluids, whose constituents chemically attract each other, come in contact, they will combine to form one mixed fluid, of which each smallest particle will exhibit a like property. If, for instance, we mix a fluid consisting of 20 parts of salt and 80 parts of water, with 100 parts of water, a fluid will be formed from the mixture, the smallest distinguishable particle of which will contain 9 parts of water to every 1 part of salt.

Precisely the same thing occurs on adding to the fluid some solid body, that is soluble in it, as salt for instance. When the solution is completed a fluid will be formed, the smallest particle of which will exhibit the same character, consisting of a definite quantity of the original fluid with a definite quantity of the dissolved body.

* For the direction of such as are desirous of entering further into this subject, I subjoin a list of the most important works regarding it:

Magnus, in Poggendorf's Annalen. Bd. 10.
N. W. Fischer do. „ 11.
Poisson do. „ 11.

Dutrochet, Mémoires pour servir à l'Histoire Anat. et Physiolog. des Végétaux et des Animaux. Paris, 1837. T. i. p. 1—99. (Dutrochet himself regards what he has written in this treatise upon Endosmosis as alone entitled to attention, considering all his former labours on the same subject, which are not incorporated in this paper, as invalid.—Avant-propos, p. xxxi.)

Kürschner, Article, *Aufsaugung*, Absorption. Wagner's Handwörterbuch der Physiologie.

E. Brücke, de Diffusione Humorum per septa mortua et viva. Dissertat. Berolini, 1842.

Poiseuille, Comptes Rendus, 1844. II., p. 994., &c.

C. Matteuci et A. Cima, Annales de Chimie et de Physique. Janvier, 1845.

Porret, Annals of Philosophy, 1816.

2.

If we suppose the two commixing fluids to be two separated masses, *a*, *b*, (fig. 1,) then the constituents of each will attract those of the other. At the same time, however, the constituents of *a* will attract those of *b*, and conversely, and this latter species of attraction is stronger than that existing between the constituents of each body among themselves. Thus, atoms will pass from *a* to *b*, and again from *b* to *a*, until both masses have become chemically equal; that is, until they have assumed a like composition.

If, in this perfect admixture of the two fluids, as much has passed from *a* to *b* as from *b* to *a*, both masses will retain their original volume after their commixture; but if, on the contrary, one mass takes up more than it gives off, the two masses will change their original volumes in such a manner that the one will have increased in proportion as the other has diminished (fig. 2). In those cases, where the two commixing fluids are contained in one common vessel, the difference of size occurring in the two masses from their admixture is not perceptible, for the mass *a* (fig. 3,) will, in accordance with the laws of hydrostatics, assume the form *a'*, when all want of uniformity in the level of the fluid will disappear. There are, however, cases in which the difference of volume in *a* and *b*, arising from their commixture, may be perceived, and where it admits of being measured; of these we will speak presently.

Fig. 1.

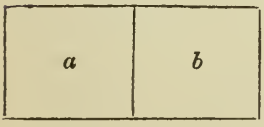


Fig. 2.

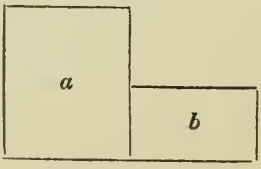
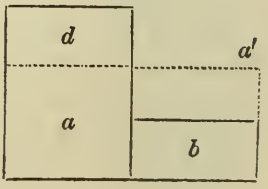


Fig. 3.



3.

Let us now consider the commixing fluids, not as two simple masses, but as consisting each of a very large number of particles, which are in each fluid perfectly similar to one another. The manner in which these particles are arranged

exercises an essential influence upon the nature of the mixture, that is, upon the time requisite for the perfect admixture of the whole. Let *a*, in fig. 4, represent a particle of a solution of salt, while the divisions from *b* to *e* are particles of water. As each particle of water must take up a definite quantity of salt in its perfect admixture, it is necessary that, in the above advanced illustration, every saline particle coming to *e* shall first pass through the particles from *b* to *d*: to traverse this course, a certain time is, however, requisite, the length of which will depend upon the length of the course to be traversed.

In fig. 5, on the contrary, where the position of the particles is different, all the particles of water being in immediate contact with the particles containing salt, the particle *e* will take up salt much more rapidly than in fig. 4.

Fig. 4.

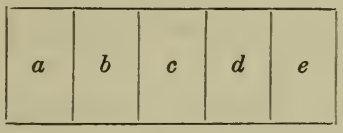
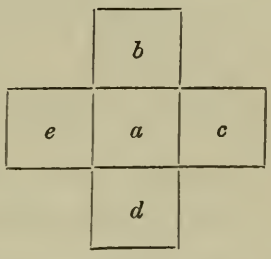


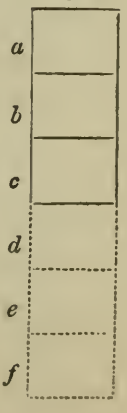
Fig. 5.



It happens, from this and similar relations, that equal quantities of fluids of the same kind, which mix together, require a very different period of time for their perfect admixture under different relations.

If, for instance, two fluids of different specific weights, which will mix together, as water and a solution of salt, spirits of wine and water, &c., be carefully brought together in such a manner that the heavier fluid shall be lowermost, the particles of both fluids being as little changed from their position as possible, the same case will occur as in fig. 4, and the perfect admixture will be very slowly effected. We may regard both masses as a column (fig. 6), the upper half of which, as from *a* to *c*, being composed of particles of spirits of wine, and the lower, from *d* to *f*, of particles of water. As long as the

Fig. 6.



particles remain at rest in their position, each atom of spirits of wine, passing from the particle *c* to *f*, must go through *d* and *e*, and, in like manner, every atom of water, going from *d* to *a*, must pass through *c* and *b*. The higher, therefore, the columns are, the longer will be the period of time necessary for the perfect admixture of the whole mass; but the case is different when not only the atoms in the two fluids, but whole portions of the mass, as from *a* to *f*, move; if, for instance, we stir them. Then each particle of water will come in immediate contact with a particle of spirits of wine, as in fig. 5. The perfect admixture will follow much more rapidly, and the height of the fluid column will not exercise any appreciable influence upon the period of time required for the perfect admixture.

The following are some of the principal causes that call forth changes of place of whole portions of matter (and not only of atoms), or, as we generally express it, *currents*, in the commixing fluids.

Mechanical forces acting from without, as *stirring*, *shaking*, &c.

The gravity, or unequal specific weight, of the commingling fluids. If, for instance, we dissolve a piece of sugar in water, taking special care to avoid every motion, it will make a great difference in the period of time required for the complete diffusion of the body in the fluid, whether we put it at the bottom of the vessel, or hold it suspended on the surface of the water. In the first case the particles of water saturated with sugar are below, and remain there owing to their greater specific weight; hence no currents will be formed, and the perfect admixture will only follow very slowly on the progression of the atoms. If, on the contrary, the sugar is above, the parts of the water saturated by it will have a tendency to sink, owing to their greater specific weight; visible currents will then arise in the fluid, and the mixture will be much more rapidly completed.

Unequal heat, *boiling*, &c., act in like manner in calling forth currents that accelerate the mixture.

As in every mixture of fluids, owing to one cause or another, currents unavoidably arise, the amount of which can-

not be accurately determined, it is scarcely possible strictly to define the difference which certain conditions occasion in the perfect admixture of two commingling fluids. Every case presented to us is a combined one, which at certain times approximates more to the condition of absolute rest, and then again at others more to that of absolute motion in the particles of the fluid. It is, however, of importance to theory accurately and strictly to distinguish these two kinds of motion, viz., *the progression of invisible atoms*, and *that of the smallest visible particles*. If, as is generally done, we term the former *currents*, we must not apply the same appellation to the latter.

4.

In the cases we have been considering, the two fluids were *miscible*, that is, they formed, in consequence of being brought in contact with each other, *one* fluid, the smallest appreciable particle of which had a perfectly homogeneous character after the perfect admixture had taken place.

There are, however, cases in which two fluids withdraw certain constituents from each other on being brought in contact, without themselves mixing together.

Thus, for instance, oil (olein) and water do not mix; and it is only after long-continued stirring that they form an emulsion, that is, a fluid in which the particles of oil and water are plainly to be distinguished from one another. If now we rub oil and common salt together, and bring this mixture in contact with water, the latter, whose particles have a greater chemical attraction for the salt than have the particles of oil, will withdraw the salt from the last-named particles, and after the perfect admixture is completed we shall have, besides the particles of oil, particles of water, each of which will hold a certain quantity of salt in solution. On mixing equal quantities of ether and water two fluid layers will be formed, which will not mix further, and of which the upper and lighter consists of ether and water in the proportion of 36 to 1, and the lower and heavier one of water and ether in the proportion of 9 to 1. On separating the two fluids, and dissolving chloride of mercury in the one, the other fluid will, on the two fluids being again mixed, withdraw a certain portion of the salt from

the solution. (Brücke.) In both cases, therefore, the one fluid abstracts from the other, without, as a necessary consequence, yielding anything in return; the one increases, and the other diminishes, in proportion to the quantity taken up.

If, in this process, we have regard to the quantity taken up in a given time by a fluid under definite relations, and to the quantity given off by the other fluid, we shall easily perceive that the quantitative amount that has passed from one to the other in a definite time is (in equal masses) greater in proportion to the surface at which the two fluids are in contact, and that it makes a considerable difference here whether the change is effected during a state of rest of the fluids, or while they are in motion (currents, § 3).

Relation of such Fluids as come in contact with Permeable Substances, or are separated from each other by Permeable Partitions.

5.

Hitherto we have considered both fluids as in immediate contact: we will now investigate the cases in which a fluid penetrates into a permeable substance, or where two fluids are separated by a permeable partition. Every substance may be regarded as a permeable partition, that admits of being penetrated by one of two fluids, or merely by certain constituents of either.

Experience teaches us that many permeable substances exercise upon the fluids penetrating into them a certain influence, which is different in different cases, and it requires therefore a special experiment for each case, to determine its nature and amount, although it admits of being brought under certain general points of view. This influence is partly *mechanical* and partly *chemical.*

6.

The mechanical influence exercised by a permeable substance upon the fluid penetrating into it consists in the fluid being attracted by the substance with a force that opposes a

certain resistance to other mechanical forces acting upon the fluid, as, for instance, gravity, hydrostatic pressure, &c.

This force is generally designated by the term capillarity, or capillary attraction. Of the numerous examples occurring of this mechanical capillary force, I will here only adduce the well-known phenomenon of water rising in a strip of blotting-paper in opposition to the action of gravity. This mechanical capillary force varies very considerably in different cases, depending (1) upon the nature (of the material) of the permeable substance and of the fluid; thus, for instance, water is attracted by all substances which it is able to moisten, whilst between glass and mercury no such attraction exists; and (2) upon the arrangement of the permeable substance, its thickness, and the size of its interstices (pores).

The many different kinds of filters furnish examples of the various manners in which this mechanical capillary force acts in individual cases. Thus, if a fluid be poured into an open funnel, it will run through much more rapidly than when it has first to pass through a filter. Its slower escape, in the latter instance, does not only depend upon the size of the openings being contracted by the solid substance intervening between the capillary spaces of the filter, but likewise upon the capillary attraction in the separate capillary spaces of the vessel, which offers a certain resistance to the hydrostatic pressure of the fluid, and thus in part removes it. In many filters this resistance is very inconsiderable, and the fluid will consequently pass rapidly through, while, in others, again, it is much stronger, and the fluid then filtrates slowly. The force of capillary attraction is, in many cases, so great that it is able to equipoise a considerable opposing force. If, for instance, a glass tube be so tightly closed by a bladder that no fluid can penetrate between the glass and the animal membrane, and if it be then filled with water, the capillary attraction of the bladder will retain the water with so much tenacity, that the pressure of a column of water several feet in height within the tube will not be able, before a period of several hours have elapsed, to force any appreciable quantity of water through the bladder, and many days, or even weeks, will intervene before a column of water, several inches in height, and whose

base covers the surface of the bladder, will be able to penetrate through the membrane. But even in the case of thick animal membranes, the resistance opposed by capillary attraction to hydrostatic pressure and other moving forces, is not, generally speaking, absolute, probably because almost every membrane between its many small pores, in which capillary attraction is very considerable, contains also several of larger size, through which fluids may be forced, even under a very inconsiderable amount of pressure.

The amount of this mechanical capillary force may be ascertained for different permeable substances by means of experiments, that at least approximate to a correct estimate; for this purpose we use glass tubes of equal diameter, which are closed with these different substances after being filled with a fluid; by this means the quantities permeating in an equal period of time by equal hydrostatic pressure may be accurately determined. Here there are, however, many relations to be regarded, which detract from the accuracy of the results obtained in most experiments of the kind. Many substances, as, for instance, the thinner animal membranes, are expanded by the pressure of the column of fluid resting upon them, and thus their efficient surface is increased, while, at the same time, their texture is changed, their thickness diminished, and their pores enlarged. When the experiments are prolonged for any length of time, the substances frequently undergo changes from putrefaction, &c.; and owing to these causes it is scarcely possible to draw any valuable conclusions from a few experiments of this nature, it being requisite to have many, even several hundred experiments, from which to derive approximatively correct mean numbers, as guiding-points for the comparison of the mechanical capillary force of different substances with each other, or with different fluids. It is, therefore, to be desired that experiments of this nature were made on many different substances, and in large numbers.

7.

Many substances that are permeable by fluids appear to exercise no further influence upon the penetrating fluid than the above-named mechanical capillary attraction. We find in

this case, on comparing the results yielded by experiments on different permeable substances, either differences only in the *time* necessary for an equal quantity of fluid of equal superficies and with equal pressure to permeate a substance, or differences *in equal periods of time* in the *quantity* of the permeated fluid. Such permeable substances do not act upon the *quality* of the fluid to change it; thus, as a general rule, we find that in ordinary filters, the permeated fluid has the same character as before it was filtered, while only such particles are impeded in their passage as are mechanically prevented by their size from passing through the pores of the filter. The matter is not, however, always so simple. Thus many permeable substances yield a passage exclusively, or in a large proportion, only to certain constituents of a compound fluid and not to others, and consequently the permeated fluid acquires a different composition from what it had when poured on the filter.

If, for instance, we pour an emulsion, composed of equal parts of water and oil upon a thick filter having minute pores, and that has been moistened by water, the latter will pass freely through, but the oil more sparingly, and the permeated fluid will contain more water than oil. We may, in this manner, deprive milk, by frequent filtration, of a large portion of its butter globules.

If putrid water be filtered through animal charcoal, many parts will be retained by the charcoal, and the filtered water will be alike devoid of odour and taste.

If bile mixed with alcohol be filtered through animal charcoal, the bile-pigment will be retained and the fluid appear colourless after filtration.

If aqueous spirits of wine be inclosed in a bladder, proportionally more water than alcohol will pass through the walls of the membrane, and evaporate, whilst the mixture remaining in the bladder will contain a relatively larger quantity of alcohol, and a smaller one of water.

If, on the contrary, we inclose aqueous spirits of wine in a caoutchouc bag, more of the spirit than of the water will escape through the walls, while the fluid remaining in the bag will contain proportionally more water and less spirit.

It would lead us too far, were we to adduce more examples

of this kind; those we have given suffice, however, to show that in many cases the fluid that has passed through a permeable substance has a different chemical composition from the one possessed by the fluid from which it was derived.

I will not here make any attempt to investigate the primary causes of this phenomenon. The result may be explained by assuming that the permeable substance in some cases chemically attracts and retains, while in others it repels certain kinds of matter, preventing their entrance into its interstices. Both cases yield so far the same result, that there is either no appearance, or but a partial one, in the permeated fluid of either kind of eliminated matter.

The simplest method of testing this chemical action of different substances on various fluids consists in suffering the latter to filter, in the manner described in the previous section, through different membranes, and examining if, and to how great an extent, the permeated fluid differs chemically from what it was previous to filtration.

We will consider somewhat more attentively, according to these general grounds, a few cases in which fluids come in contact with permeable partitions.

8.

One of the simplest cases is, that in which two like fluids are separated from each other by a permeable partition. If the hydrostatic pressure be equal on both sides no change will occur. If, on the other hand, the pressure be stronger on the one fluid, a certain quantity of this latter will pass over to the other fluid. This quantity will correspond to the excess of pressure on the one side, allowing for the resistance opposed to the pressure by the mechanical capillary force. Here, however, we presuppose that the partition exercises no specific chemical action on the fluid, but suffers it to pass unchanged. The final result of the process consists, therefore, simply in this, that the one fluid gives off a certain quantity to the other without receiving anything in return; that is, the volume of the one fluid increases as that of the other correspondingly diminishes.

If, on the contrary, a specific chemical action of the

partition also come into play, that is, if the permeated fluid have a different property from that on either side of it, the two fluids will be chemically different, and the case then becomes more involved, ranging itself in a class with others which we shall subsequently consider.

9.

Another tolerably simple case presents itself where a fluid is on one side of a partition, and on the other a substance attracting this fluid without being dissolved in it.

If, for instance, we fill a clay cell, or a glass tube secured by some animal membrane, &c., with blotting paper, dried sponge, or with dried animal or vegetable matter, fibrine, coagulated albumen, resin, mucus, &c., and put it into a vessel filled with water, the water will penetrate through the partition and pass from its inner surface to the substance chosen for the experiment, causing it to swell.

Here, too, the permeation is limited to one side; that is to say, parts of the fluid pass through the partition without the fluid itself receiving anything in return. The quantity of fluid which passes through the partition in a given time depends upon the superficies of the latter, and upon the greater or lesser energy with which the substance in the interior attracts the fluid without the partition, and likewise upon the quantity of that substance.

The *quality* of the permeated fluid depends, (1) upon the chemical influence of the partition on the given fluid. The inner surface of the partition will only present to the substance the fluid capable of passing through it: (2) upon the chemical power of attraction exercised by the substance itself upon the individual constituents of the fluid presented to it by the partition.

We may also consider these cases as if a fluid were imbibed by a permeable substance consisting of layers of different natures (as a partition and inner substance,) and may thus avail ourselves of them, in order, by a careful chemical investigation of the fluid imbibed, (which may be obtained here in a larger quantity,) to decide upon the chemical capillary action which different substances exert upon compound fluids.

10.

The cases are more involved where two fluids of different character, capable of being mixed, are separated by a permeable substance. Here, owing to the mutual chemical attraction exercised by the constituents of the one fluid on those of the other, both fluids will strive to become chemically equal, (see 1,) and this perfect admixture will always succeed as the final result of their being brought in contact, although in a shorter or longer period of time and attended by different accessory circumstances, whilst the volumes of the two fluids may either remain unchanged, or the volume of the one increase as that of the other diminishes.

The only truly practically important point to be traced out in the arrangement of all experiments on this subject may be embraced in the following simple question: *Which constituents of the fluid A (as well with respect to quality as quantity,) pass in a given time to B, and which pass from B to A?* When we have ascertained this, we know not only what is the chemical composition of both fluids after their reciprocal action has continued some time, but likewise the amount of their volumes, by which we learn whether the one fluid has taken from or given to the other, or whether both have retained their volumes unchanged. Conversely, however, this question may be easily answered by a quantitative chemical investigation of the two fluids with respect to their absolute amounts, and it is much to be regretted that the experiments hitherto made upon the so-called Endosmosis have been directed almost exclusively to the investigation of the changes occurring in the volumes of both fluids, although this really only forms one single point of the whole process, while little regard has been paid to the quantitative changes occurring in fluids.

The above question can only be answered by an experiment for each individual case, and as every single experiment, for the reasons already given, yields results which, in spite of the greatest caution, are not precisely alike in all cases, the answer must be sought in many experiments, rather than in a single one. In this respect there is still a great hiatus to be filled up, and individual experiments, and even individual series of experi-

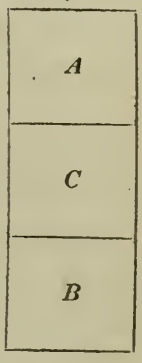
ments, afford such unsatisfactory results, that I omit giving the data derived from a course of observations I pursued with respect to the mixture of solutions of salt and water, and of various salts in water.

Certain general considerations may, however, be combined, serving partially to explain the results of many experiments, and partially to enable us to determine beforehand some few at least with an approximation to the truth.

The cases appertaining to the chemical mode of action of the partition may be divided into three classes.

1. The partition may exercise no chemical action upon the fluids: both permeating the substance freely, and then mixing within it. The chemical composition of the fluid within the substance of the partition, (fig. 7) will then be the simple result of the reciprocal chemical action of the two original fluids (*A* and *B*, fig. 7). The partition takes no other part in the mixture than by means of the mechanical capillary force it exercises: considered from this point of view, the mixture is effected precisely as if both fluids were in one common vessel (see 1 to 3).

Fig. 7.



2. The partition may only suffer the constituents of one of the two fluids to pass through it. The fluid within the partition (*C*, fig. 7,) will then have the same composition as one of the fluids ($c = A$ *or* B). The result is similar to what was spoken of at 4, where salt is brought in contact with oil and water, or as at 9. Only such constituents as are able to penetrate the partition pass from *A* to *B*, but not conversely from *B* to *A*.

3. The partition may admit of the passage of the constituents of both fluids, but in unequal proportions. *C*, therefore, will have a peculiar composition, different to that which it would have possessed, if *A* and *B* were directly mixed.

The further process is the same in all three cases, and consists in *C* becoming identical with *B* as well as with *A*, in accordance with the laws that obtain concerning the mixture of fluids in common vessels, and this continues until all parts of *A*, *B*, and *C* are in a state of perfect chemical and mechanical equilibrium.

Let us consider somewhat more attentively a few cases of this kind.

The most simple are those that have been spoken of under the head 2. *C*, (fig. 7) = *A*, is attracted by *B*; a portion of the former will therefore pass over to *B*, without, however, any part of *B* conversely passing to *C*. What is lost by *C* is again supplied by *A* forcing itself in, and this newly acquired portion of *A* passes again to *B*, until finally the whole of the fluid *A* will be conveyed to *B*. The latter, therefore, has been augmented by the whole mass *A*, and has the same composition as if *A* and *B* had been immediately mixed, provided always that the force with which the partition retains a portion of *A* in *C* be not greater than the force with which this portion is attracted by *B*. We have not many opportunities of observing pure cases of this kind in nature: almost all permeable partitions of this species contain large pores through which some portion of *B* may penetrate, so that instead of all the fluid passing to *B*, a quantity of a mixture of *A* and *B* will be found in *A*. Amongst cases of this kind, we may mention the one in which water and spirits of wine are separated by an animal membrane or by a caoutchouc plate, or that in which there is water on one side of the partition, and gum, mucus, or some other insoluble animal or vegetable substance on the other.

In the cases belonging to the first and third class, *C* is a mixture of *A* and *B*, and will therefore give off constituents from *A* to *B* as well as from *B* to *A*. It now depends partly upon the nature of *C*, and partly upon the amount of attraction reciprocally exercised by the separate constituents of *A* and *B* on each other, whether more will pass from *A* to *B*, or from *B* to *A*, or whether equal quantities will go to both sides; the result will, therefore, differ very much in different cases, and the confirmation of this law of transition for different partitions and different fluids can only be arrived at by practical experiments.

A few laws of this nature may be derived from the results yielded by the numerous experiments of Dutrochet. Thus, for instance, we know, that when concentrated solutions of salts, gums, albumen, and other substances, mix by means of an animal membrane with water, or with diluted aqueous solutions of their own nature, more of the water will pass to

the salt-solution, and generally from the diluted to the concentrated fluids, than conversely, and consequently as the water diminishes in bulk, the solution will increase. The increase of volume of the concentrated fluid is, however, more considerable in proportion to the difference in the degree of concentration of the two fluids. When distilled water and a very concentrated solution of salt mix through an animal membrane, more water will pass to the salt, than if the water and a weaker solution of salt be separated by a membrane of like nature.

The contrary is the case with most acids when not too concentrated: on their mixing with water through an animal membrane, more of the acid will pass to the water than conversely; the volume of the acid consequently diminishes.

The quantities of matter passing in an equal time from *A* to *B* and from *B* to *A*, depend (other relations being the same) upon the extent of the superficies of the partition; the larger this is, the more will pass through it, and conversely.

The motion or rest, of the two fluids, exercises also an essential influence upon the quantity of that which passes in equal periods of time. This quantity (other relations being the same) is greatest when both fluids are in continued motion (see 3).

The nature of the membrane is of the greatest moment: all influences affecting its chemical and mechanical capillary forces, diminish for the same reason the relations of the mixture of the fluids that are separated by it. Most animal membranes are composed of different layers, which not unfrequently possess different capillary forces; it is not, therefore, always a matter of indifference as far as the result is concerned, whether one superficies of the partition be turned towards the one or other of the fluids, and of this we have evidence in the experiments of Matteucci and Cima. These circumstances all combine to make the phenomena exhibited in the mixture of substances by means of permeable partitions very much involved, rendering it extremely difficult to draw any previous conclusions as to what may occur in a certain case.

Let us now endeavour to apply a few of the results obtained to the processes in the human organism.

Many phenomena in the human body depend exclusively

upon the permeation of fluids through organic partitions, while in other phenomena this process plays a more or less important part. In endeavouring in the following pages prominently to bring forward a few examples appertaining to this class, my principal aim has been directed to the furtherance of this object, which is of the greatest importance to physiology and pathology, urgently recommending the pursuit to others, as a labour of too exhausting a nature for the cultivation of one alone.

In the first place, it is clear, that whatever the body takes up from without as a means of nutriment, in the widest sense of the word, can only reach the interior of the body by passing through animal membranes in the condition of a fluid. I do not speak here of the gases, that entering the lungs and the external skin, pass thence into the blood-vessels and the inner parts of the body, but will limit myself especially to the consideration of those means of nutriment which enter the stomach in the form of food and drink, and are then dissolved as far as they were not already fluid and resorbed. How are we to regard this resorption?

The food we partake of passes first through the mouth, the fauces, and the œsophagus. All these parts are covered by a thick epithelium, which does not readily yield a passage to fluids. In the stomach, however, whose walls permit fluids to pass more readily through them, an energetic reaction takes place between its fluid contents and the blood flowing through the gastric vessels, and this process is continued throughout the whole length of the intestinal canal. The contents of the stomach are usually much more aqueous than the blood: the various kinds of drink, and most articles of fluid food, are naturally so; and concentrated food becomes so by being mixed with the aqueous saliva and gastric juice. As is usually the case where a concentrated fluid comes in contact with one that is more aqueous, there is no doubt a larger quantity of the thinner fluid passes through the membranous partition to the concentrated, than conversely. Thus, by degrees, a larger portion of the contents of the stomach and of the intestinal canal (both water and the substance it holds in solution,) is conveyed into the vascular system than, on the other hand, passes from the

blood to the fluid of the digestive canal, as has been directly shown by the experiments of Poiseuille. We are still deficient in exact researches respecting the substances that pass from the blood-vessels to the contents of the intestinal canal, but they are probably salts with a small quantity of extractive matters and some protein compounds, which latter are then converted into mucus. What is usually denominated gastric and intestinal mucus is doubtlessly the equivalent yielded in the act of digestion by the blood to the contents of the stomach and the intestinal canal, but it will, of course, be understood that gastric and intestinal mucus may be secreted by the blood, in the manner we shall subsequently consider under the head of secretions, without that fluid receiving anything in return. It is, however, arranged in the most wonderful manner that almost the whole contents of the stomach and intestinal canal may gradually permeate into the interior of the organism, without any appreciable quantity of matter on that account passing as an equivalent from the blood to the digestive canal. In the first place the acid character of the gastric juice seems to be of great importance. Thus, we learn from the experiments of Dutrochet that acid fluids, especially in mixing with another fluid by means of an animal membrane, yield more than they receive from the fluid, and thus the acid character of the contents of the stomach seems to be precisely the means by which resorption is promoted in a simple physical manner. It would be, however, highly desirable to institute a series of carefully conducted experiments on the probable influence of the acid in the gastric juice on the resorption of the chyme. This latter exhibits its acid property not only in the stomach but also at the entrance of the small intestines, and retains it through the great portion of the passage through it. We consequently see that this aid to the resorption of the chyme is not limited to the stomach alone.

The more two fluids separated by an animal membrane differ in their degree of concentration, the more proportionally will the concentrated take up from the thinner fluid. The passage of the nutriment into the blood is, therefore, essentially promoted by the commingling of other watery juices, as, for instance, the bile and the pancreatic fluid, to which may be added,

the gratification of the desire to drink that is generally felt soon after eating, and thus contributes to the dilution of the contents of the stomach. The bile contains in itself much more water than the blood; consisting, on an average, of about 10 per cent. of solid constituents, while the blood contains more than 20 per cent. The bile, however, becomes yet more aqueous in the intestinal canal, owing to a portion of its solid constituents (the bilate of soda) being decomposed by the acid of the chyme, and separated in a partially modified condition as an insoluble substance, dyslysin, &c. It contributes, therefore, essentially to the dilution of the chyme, facilitating its resorption. In like manner the pancreatic fluid acts, which, although we know but little of its composition, is, at all events, much more aqueous than the blood (containing about 8 per cent. of solid constituents). Another means, acting with the same object, is the circulation of the blood, the consequence of which is, that the portion of blood become more dilute by the resorption of aqueous particles from the chyme, is constantly removed and replaced by more concentrated blood. Owing to all these relations, an augmented difference is brought about in the concentration of the chyme and of the blood, and the largest part of the food is thus conveyed from the intestinal canal directly into the blood-vessels, without an equally large quantity of the contents of the latter being transferred to the intestinal canal. Numerous experiments require, however, still to be carefully conducted regarding this point, with special reference to the question, whether *all* constituents of the chyme pass alike readily into the blood, or whether there is a difference in this respect.

In the meantime, notwithstanding these arrangements, and especially after partaking of solid or very rich food, a portion of the chyme will often remain in so concentrated a condition in the intestinal canal that no part of it can pass into the blood-vessels through an interchange of their contents. Special provision is made for these cases by means of the *chyle-vessels*, or *lacteals*. Whatever may be conjectured concerning the origin of these vessels, so much is certain, that they arise from cavities in the intestinal villi which do not communicate with the intestinal cavity by open mouths, but are separated from it

by a membranous partition,—mucous membrane with epithelium. The passage of the contents of the intestinal canal can, therefore, only be effected by a penetration through this partition. Here, again, we find different arrangements tending to promote the passage. In the first place, the chyle-vessels after fasting are filled with a fluid, lymph, which, although less concentrated than the blood, is more so than the chyle, and, like the blood, draws more from it than it yields. This, however, is only a secondary agency, and the chyle-vessels stand far below the blood-vessels in the active exercise of this function. A second, and far more efficient agent, which transfers the fluid part of the contents of the intestines into the chyle-vessels, and then conveys it further on its course, is of a *mechanical* nature. By the peristaltic action of the intestinal canal (the contraction of its muscular coats) so considerable a mechanical pressure is exercised upon its contents that a portion of them (in a fluid condition, of course,) is forced through the walls of the intestines, and conveyed into the chyle-vessels to be again propelled onward. As the valves of the chyle-vessels prevent the return of the chyle on the cessation of the peristaltic motion of the intestinal canal, the portion of the chyme which, owing to its concentration, could not pass directly by diffusion into the blood, is, in this manner, circuitously conveyed into the vascular system. It follows, therefore, that, on the occurrence of deficient or abnormal contraction of the intestinal canal, that the part of digestion which depends upon resorption through the chyle-vessels must suffer a disturbance.

The chyle-vessels further aid in the process of digestion by serving for the resorption of fat. Fat does not mix with water, and as it can either not at all, or only with difficulty, pass through membranes moistened by aqueous solutions, it cannot penetrate in more than a very small quantity from the chyme into the blood-vessels. Fat may, however, penetrate from the intestinal canal into the chyle-vessels, as has been shown by experiments made on the chyle of animals which have been killed soon after partaking of fatty food. The permeation of fat through the intestinal walls into the chyle-vessels is no doubt effected in the same way that oil penetrates

through a filter moistened with water; thus, in some parts of the filter, the water is displaced by the long contact with particles of oil, so that the filter becomes saturated in these parts, and thus forms, as it were, bridges for the passage of the succeeding particles of oil, which are driven over in the same manner as the aqueous parts of the chyme are forced by mechanical pressure into the chyle-vessels. Fat, therefore, is not dissolved by the action of a digestive fluid, but the solution is effected by the heat of the body, and fatty mixtures whose fusion-point is above 40° C., are either not at all digested, that is resorbed, or only gradually dissolved by the agency of more fluid fat subsequently taken into the system by food. In the resorption of fatty food, the surface of the intestinal canal divides itself, as it were, into two parts, of which the one resorbs aqueous chyle, and the other fat. The digestion of fatty food is more slowly effected than that of aqueous substances, owing to the time required by the fat to force the water out of the walls of the separate villi. The resorption of aqueous fluids is rendered more difficult, when fat has been partaken of on an empty stomach, as the fat deposits itself upon the surface of the intestinal canal, covering it with a coating of oil, which hinders the entrance of the water. This explains the reason of the inconvenience experienced on partaking copiously of water after eating fatty food, and, in like manner, why the effect of intoxicating drinks, as ale, for instance, may be retarded for some time by taking a few spoonsful of oil on an empty stomach.

A physiological consequence derived from the views previously given with reference to the resorption of alcohol, is worthy of remark. If alcohol be diffused with watery fluids through animal membranes, only a small portion of the spirit will pass to the water, while a great deal of the latter will go over to the spirit. This evidently indicates that spirits of wine, when taken into the stomach in a highly concentrated condition, can only reach the blood slowly, and in a diluted state. Thus, the spirit cannot possibly retain its usual action of coagulating albumen, after it has entered the blood of the living organism.

In certain cases, the resorption of food and drinks in the

intestinal canal is impeded by the action of medicines. This in the case with salts, for instance, which almost all have a purgative action, and arises from the fact, that concentrated saline solutions take more from the fluid of the blood in passing through animal membranes, than they yield to it; this again has been directly shown by Poiseuille, although, as in the case of other points, accurately conducted experiments and observations are still required to determine what are the substances that pass from the blood into saline solutions, and in what relations the exchanges occur. Opium, as is well known, checks diarrhœa; and this phenomenon, according to Poiseuille's investigations into the subject, admits of being explained by the changes effected in the capillary forces of the coats of the intestines; thus on the addition of opium to a saline solution, which is thoroughly diffused with the serum of the blood by means of an animal membrane, contrary to what is the case before the opium is added, more of the saline solution is attracted than is given off; but here again we must regard further chemical investigations as highly desirable. Probably, at some future period, when experiments have been more fully pursued regarding this point, many other actions of medicines upon their resorption in the intestinal canal will have to be referred to the above-named phenomena of diffusion.

It is only such constituents of the contents of the intestinal canal as are dissolved which can be resorbed; all undissolved or insoluble matter passes off with the excrements. This seems to be so clear, that I should not have deemed it necessary to speak of it, were it not, that in recent times some physiologists have maintained the view, that even undissolved substances might penetrate, when reduced to the condition of the finest particles, into the (non-existing) open mouths of the chyle-vessels.

In the occasional instances where the external skin has reorbed liquids by means of baths or frictions, the case is precisely the same as in the intestinal canal, only that here, owing to the greater thickness of the epidermis, the action is less energetic, so that resorption is principally limited to those parts, where the epithelium is thinnest; as, for instance, in the numerous glands of the skin.

We will now consider the processes, in which fluids pass by diffusion from the interior of the organism—processes which are usually designated by the term *secretion.* I will here again limit myself to liquids, as the laws according to which elastic fluids are diffused through liquids, as for instance, in the process of respiration, are still less known.

One of the simplest of these processes is the *transpiration* of the skin, and the secretion of *sweat.*

The former evidently arises from the skin, that is to say, the cutis and the under layers of the epidermis, (the so-called rete malpighii) being saturated with a fluid, originating from the blood, and of which a certain quantity, composed of water, with gases and other volatile constituents, evaporates in the air, whilst the non-volatile constituents remain. In the formation of *sweat,* we have an opportunity of collecting this fluid in a larger quantity, and of examining it to compare its composition with that of the blood, from which it is evidently derived. There is, however, this great difference between the two, that sweat is very much more dilute than blood, containing besides the water only a small quantity of salts and extractive matter. We must consider somewhat in the following manner the many agents which contribute towards its formation. Its primary source is the blood, which everywhere in the vascular system is exposed, owing to the contraction of the heart, to a greater hydrostatic pressure than the fluid in the cellular tissue, &c. Thus, a certain quantity of the liquor sanguinis passes constantly out by means of the walls of the vessels, this quantity corresponding to the excess of hydrostatic pressure in the vessels over that of the external fluids, minus the mechanical capillary force of the walls of the vessels. The chemical composition of this fluid depends upon the chemical capillary force of the walls of the vessels, that is to say, it is changed into a modified form of liquor sanguinis. Whilst this fluid presses to the upper surface of the skin into the lumina of the perspiratory glands, it must permeate through other organic partitions, the tissue of the cutis, the walls of the perspiratory glands and their epithelium. These, however, act upon it in such a manner as to change it; that is to say, they suffer some of its constituents to pass more easily than others, owing to which causes the com-

position of sweat differs considerably from that of the liquor sanguinis, from which it is derived. We will endeavour to follow these relations more thoroughly in several individual cases. In the first place, it is evidently of great consequence to know how the fluid is composed which escapes from the blood through the vascular walls, and which, owing to its being distributed in every direction where the blood-vessels are ramified, I will designate by the name of the *general nutrient fluid.* It will be seen at once that its character is dependent upon several conditions: 1. On the character of the blood. 2. On the character of the vascular walls, that is, upon their mechanical and chemical capillary forces; it is, therefore, probable that it may differ in the veins and in the capillary vessels; and it is further possible, that different capillary vessels, even in their normal condition, admit of the passage of a different fluid through their walls. 3. Its character doubtlessly depends upon the relations of pressure in the vascular system, so that a vascular wall that is very much thickened and contracted, will admit of the passage of a different fluid from what is transmitted through a very relaxed wall. But as the relaxation and contraction of the vascular walls depend upon the nervous system, we perceive the important influence exercised by the latter upon the secretion. As yet we unfortunately know but little that can be relied upon regarding the influence of all these relations on the character of the permeated fluid, and a wide field is thus opened to us in which great and lasting services may be rendered to science by the earnest pursuit of a series of carefully conducted experiments. From a comparative consideration of the composition of different normal and pathological fluids, which may be regarded as more or less changed nutrient fluid, as lymph, serum of pus, inflammatory exudations, &c., we learn that the general nutrient fluid forced by the hydrostatic pressure of the blood from the capillary vessels, contains essentially the same constituents as the liquor sanguinis, although in a different proportion. It generally contains more water, somewhat more of extractive matters and salts, but on the other hand, less of the protein compounds (albumen and fibrin) than the liquor sanguinis. The fluid which passes through the walls of the veins (serous dropsy),

appears to differ from the general nutrient fluid by the absence of fibrin. It may also, as experience testifies, suffer considerable alterations in its character, either owing to dilatation or contraction of the vessels, or from changes occurring in the blood, but as yet our knowledge is very deficient on this head.

Let us now turn from the consideration of the general nutrient fluid to that of the formation of *sweat.* Sweat is ultimately derived from this fluid, which is far more dilute than the liquor sanguinis, containing more salts and extractive matters, and less of the protein compounds, than the latter. Before this fluid reaches the perspiratory glands it experiences a second filtration through the substance of the cutis, and the walls and the epithelium of those glands. The latter retains certain constituents of the nutrient fluid (as the protein compounds, converting them to their own epigenesis and nutrition,) and a portion of the salts; in return they probably give off to the permeating fluid a small quantity of matter produced by their chemical process of development; as, for instance, extractive matters. The sweat consequently differs very considerably in its composition from the liquor sanguinis, containing, besides water, only a trifling quantity of salts and extractive matters. Sweat may assume a different composition owing to pathological causes, partly from the changes thus effected in the capillary relations of the blood-vessels (when, consequently, an abnormal nutrient fluid will be secreted), and partly owing to the changes occurring in the capillary relations of the skin and the epidermis. There exists a certain similarity between the conditions of the formation of sweat and those of the different pathological fluids which we observe to make their way through the skin, as the contents of blisters produced by burns, cantharides, pustules, bullæ, &c. On removing the epidermis, a portion of this fluid is converted into pus, owing to the fact that the protein substances which, in the normal condition, contributed to the regeneration of the epidermis, are now spontaneously developed into pus-cells.

The lachrymal secretion is precisely similar to the formation of sweat. Here, too, the secretion, which doubtlessly originates from the blood, or the general nutrient fluid, is so

modified in its passage through the walls of the lachrymal glands and their epithelium, as to consist almost exclusively of water, with a small quantity of salts and extractive matters.

Besides the mere discharge of fluids from the blood by diffusion, a new agent is added to most secretions. Thus a portion of the permeating fluid is modified by an organo-chemical process, and mixed in this altered form with the secretion. This is most plainly shown in the secretions of the reproductive organs,—in the testicles and ovaries,—where this portion forms the principal mass of the secretions. Thus, for instance, in the testicles by the fluid passing into the secreting canal, and doubtlessly from its protein compounds, organised structures, the seminal filaments, or spermatozoa, are developed, which, together with the remaining fluid, constitute the secretion.

A very general product of this kind, occurring in almost all secreting canals, is *mucus*. It is formed upon all mucous membranes, that is to say, upon all very vascular surfaces covered with a thin epithelium. Its origin may probably be explained on the hypothesis that the more scanty cells of the epithelium do not, like the numerous layers of the epidermis, consume the whole protein contents of the secretion in their own nutrition, but leave a portion which, combined with salts and alkaline bases, passes onwaids in a modified form; composing a mucous investment to the secreting canal. The common law, as it may be termed, according to which the protein substances disappear that had passed during the normal secretion from the general nutrient fluid to the secreting canal (being either converted into mucus, or applied to purposes of nutrition), further explains the fact, which at first sight appears so paradoxical, that no secretion (with the exception, perhaps, of the pancreatic fluid,) contains, in its normal condition, coagulable albumen, whilst both the blood and the nutrient fluid are so rich in this substance.

Milk alone affords an exception to this rule. It contains no albumen, but casein, which, as Scherer showed, is only a modification of albumen produced by combination with alkaline bases. The mammary gland exhibits so many peculiarities in the character of its secretion, that we will devote some little

time to its consideration. In the first place, its secretion is highly concentrated, (containing, on an average, 15 per cent. of solid constituents,) and it thus approximates more to the character of the blood, forming a strong contrast to the highly dilute secretions of sweat and tears. The walls of this gland admit of the passage of the nutrient fluid in a highly concentrated condition, but exercise such an influence upon it as to convert the albumen into casein, that is, by combining it with alkalies. This, doubtlessly, is first effected by the action of the cells.

Another peculiarity in this gland consists in its taking up fat and extracting it from the blood. This action likewise seems to originate in the glandular cells, where fat is attracted, and after being dissolved within the cells is liberated, and then mixes with the milk in the form of globules. Although not impossible, it seems very improbable to me that fat should be first formed in the mammary gland from other substances.

Other glands, as the sebaceous glands of the skin, viz., those in the axillæ, the glands of the generative organs, and the ceruminous glands, likewise possess the property of attracting fat from the blood or the nutrient fluid. If once such a gland be filled with fat the latter substance will, owing to physico-chemical grounds, exclude the passage of aqueous fluids, and the gland will then only take up fat. The fatty cellular tissue in the parenchyma of the body appears to have the same property.

The *salivary glands* stand at a medial point between the perspiratory and mucous glands. Their secretion is very aqueous, containing scarcely 1 per cent. of solid constituents, and besides water exhibits only a small quantity of salts and extractive matters, the protein compounds of the permeating nutrient fluid being converted into mucus.

It still remains to be proved whether the salivary matter contained in this secretion had existed in the blood, and been attracted in a perfectly developed form in the glandular cells, or whether it is formed within the glands by the chemical action of the cells.

The *glands of the stomach* exhibit many peculiarities: the product of their secretion so far coincides with the saliva that

it contains watery fluid with salts and extractive matters, while the remains of dissolved glandular cells testify to the presence of protein consumed and changed by organization. But the gastric juice exhibits the peculiarity of containing a free acid. The manner in which this acid is conveyed to it is so much the more difficult to understand, that we do not even well know its chemical character, for as this acid was formerly regarded as hydrochloric acid, it has been supposed by more recent investigations to be lactic acid, combined with a little phosphoric acid, which latter, however, simply owes its origin to the action of the lactic acid upon the alkaline phosphates simultaneously present. By what means is the presence of this free acid brought about? The answer to this question is not easy, and many conjectures may be hazarded on the subject. The acid owes, without doubt, its origin to the blood, and the process of its formation may be owing to the decomposition of certain salts of the blood, (alkaline lactates or chlorides) by the cells of the gastric glands which retain the acid, whilst the alkali returns by diffusion into the blood. As the cells gradually become broken up and dissolved, the acid is liberated and mixes with the gastric juice.

The opposite to this occurs in the liver, whose secretion contains soda combined with a weak organic acid, bilic acid. The processes in the secretion of the bile are not clearly understood, principally because we do not know whether the biliary matter is contained as such in the blood, or whether it is first formed in the liver. Either may possibly be the case, and we may thus with tolerably equal grounds of justification oppose to each other two different views concerning the origin of the bile. The constituents of the bile may be contained as such in the blood. This appears certain with respect to some of them, (as, for instance, the bile-pigment,) which are attracted by and enter the hepatic cells, and by their solution these constituents are liberated, and with the fluid which passes from the liquor sanguinis by diffusion into the biliary ducts form bile. Or we may suppose that the fluid entering the biliary canals of the liver is first converted into bile by the chemical activity of the hepatic cells, when, probably, many products of these metamorphoses are returned to the blood by diffusion in conse-

quence of the reciprocal action exercised upon each other by the bile and the blood of the hepatic capillaries.

It still remains for us to consider *the urinary secretion.* The urine consists in the first place of a very aqueous fluid, composed similarly to sweat, of water principally, with some few salts and extractive matters, which passes by diffusion from the blood into the urinary canals. It contains, however, additionally, specific substances, as urea, uric acid, hippuric acid, and their salts, and colouring matter, and these, at least with reference to the quantities in which they occur, are peculiar to the urine. These substances are certainly present in the blood, but the quantity in which we find them here, renders the assumption probable that owing to a peculiar power of attraction inherent, no doubt, in the glandular cells of the urinary canals, they are attracted by these from the blood into the cells, and thus passed into the urine.

According to the explanations given by Bowman regarding the histology of the kidneys, we may represent the matter to ourselves somewhat in the following manner.

In the malpighian bodies, that is, in the vascular loops which penetrate immediately into the entrance of the urinary canals, an aqueous fluid, holding salts in solution, forces itself through the walls of the renal vessels into these tubes. In its further course through these canals, the peculiar constituents of the urine, as uric acid, hippuric acid, colouring matter, urea, &c., are taken up in large quantities by the cells from the blood, and either pass into the urine by the disintegration of these cells, (by which they are liberated) or are taken up from the glandular cells of the urinary canals by means of the above-mentioned watery fluid originating in the malpighian bodies.

The blood-producing glands, as the spleen, the supra-renal capsules, thymus, and thyroid, also manifest peculiar relations. Substances occur in them, which passing by diffusion from the blood, undergo many modifications in the glands themselves, as, for instance, by cellular formation, and after being to a certain extent modified, are again returned to the blood by diffusion.

We may thus, in a great measure, deduce the peculiarities of almost all the secretions from physical and chemical relations, and there are, therefore, grounds for hoping, that at no very

remote period, when organic chemistry shall have made further advances, we may learn to know many of these processes in their normal and pathological relations.

The two widely diffused processes of the absorption of the nutriment and of secretion are not, however, the only ones in the organism in which diffusion of fluids plays a prominent part. They are merely the two visible and extreme members of a long series of processes, which are connected together like the links of a chain. Everywhere in the interior of the body similar phenomena are continually occurring, which, however, owing to their multifarious forms, and the constant change of the conditions on which they depend, do not admit of being pursued in detail, but must be simply sketched in their rough outlines. All portions of the body are saturated with this general nutrient fluid, of which we have already spoken. The first condition requisite to its secretion is an excess of hydrostatic pressure in the blood-vessels, by which a portion of the liquor sanguinis modified by the mechanical and chemical forces of the vascular walls, is forced out of the vessels. If, on the one hand, the composition of the blood, and, on the other, that of the nutrient fluid, remain unchanged, while the mechanical and chemical capillary forces of the intervening vascular walls are likewise the same as before, both fluids will soon be brought into a condition of equilibrium and cease to act further upon each other.

These relations are nevertheless subject to continual fluctuations in every part of the body. In the first place, the nutrient fluid is constantly changed by the tissues with which it is brought in contact. These are incessantly depriving it of some of its parts, at the expense of which they increase, decomposing others, and contributing new ones—the products of their own chemical metamorphoses. Thus, the nutrient fluid is ever being chemically changed, and hence follows naturally a continual new chemical admixture with the fluid contents of the blood-vessels. Another agent ever at work in altering the relations of equilibrium of these fluids is of a mechanical nature. The hydrostatic relation of equilibrium existing between the liquor sanguinis and the nutrient fluid is dependent, on the one hand, on the pressure of the blood in

the vessels, and, on the other, on the pressure to which the general nutrient fluid is subjected. As the pressure of the blood in the vessels undergoes constant change from the influence of the vaso-motor nerves, occasioning dilatations and contractions of the vessels, and then again from the alternating contractile action of the heart, the hydrostatic pressure upon the nutrient fluid is likewise of an alternating character. It is continually changed by the local contraction or relaxation of the muscles and other contractile tissues, by temporary relaxations and contractions of the lymphatic vessels, which either give a free passage to the nutrient fluid (lymph) flowing into them by diffusion, or momentarily retain it, and thus increase the hydrostatic pressure. Another agent of change is afforded by the alternating property of the blood. This fluid, parting first with its watery constituents in the organs of secretion, becomes, in consequence, more concentrated, and then again, taking up water in the intestinal canal, is rendered more dilute; the character of its chemical composition being thus liable to greater or lesser changes at every moment in every part of the body. As now all these agents, that are at one time constant and lasting, at another periodically variable, are continually changing in their degree of intensity, a source is opened to the motions of diffusion in the fluids of the body, which, sometimes inclined in one direction, sometimes in another, are never at rest, and manifest their presence by keeping up that constant molecular progression of the fluids which is essentially necessary to the stability of life as the basis and auxiliary of the metamorphosis of matter, but which not unfrequently becomes the cause of disease.

To those already considered we might add other motions of diffusion, which without being in immediate connection with the circulation of the blood and the lymph, occur between the various cells, whilst the fluid contained within each individual cell constantly modified by chemical metamorphoses, endeavours, by changes of its mechanical and hydrostatical relations, to bring itself into a state of equilibrium with the parts surrounding it, in which it is, however, continually disturbed by the intervention of new causes.

These considerations might be carried out much more in

detail, and would admit of being exemplified by many illustrations, did I not deem it superfluous to enlarge further upon the subject. My main object was simply to draw attention to those important phenomena of the diffusion of fluids in the body, which together with the molecular chemical processes constitute the great department of the metamorphosis of matter, and to encourage others to institute a numerous series of experiments, and collect materials in larger quantities than we have as yet possessed them, in order to enable us to give an exact and mathematical basis to our labours in a region of darkness, that has hitherto been solely occupied by vague hypothesis.

IV.

REPORT.

UPON ISOMORPHISM.

By Professor Otto, *of Brunswick.*

Gay-Lussac was the first who made the observation that a crystal of potash-alum on being put into a solution of ammonia-alum, continues to increase without changing its form, and that we may therefore cover this crystal with alternate layers of the two kinds of alum without injuring its regularity or its original form. Beudant subsequently found, that a mixed solution of sulphate of copper and sulphate of iron would give crystals, having the form of the latter, but still containing a considerable quantity of copper. Mitscherlich was, however, the first who by means of his investigations into the crystalline forms of chemical compounds, observed an identity of form in a sufficient number of cases, to determine that this was the consequence of a similarity in composition. He termed this similarity in crystalline forms *isomorphism* (from *ἰσος like*, and *μορφη form*), and the bodies which assume one and the same form, he named *isomorphous* bodies. The law from which this is derived is as follows:—*from an equal number of atoms, similarly combined, a crystal of like form is produced.* The crystalline form is dependent upon the number and the relative position of the atoms, and not upon their chemical nature.

We may easily perceive, that if this law admit of general application, the crystalline form must give an extremely im-

portant aid in the judgment of the atomic constitution of chemical compounds. For if equal numbers and like arrangements of the atoms produce like crystalline forms, two compounds of the same crystalline form must have a like atomic constitution.

The law is not confirmed in its full extent, and it has also hitherto been impossible to follow it through the whole series of elements, since the cases of comparison are circumscribed by the disinclination shown by certain groups of elements to enter into combinations, whose composition is perfectly similar to that of the combinations of other groups.

In the year 1839, Kopp discovered the connexion of isomorphism and the equivalent volume, (atom-volume,) and showed definitively in 1840, (*Annal. der Chem. und Pharm.*, bd. 36, s. 1,) that *isomorphous bodies have the same equivalent volume*, or, in other words, that, in isomorphous bodies, the specific gravities stand in the same relations as the equivalent weights,—or that *equivalent quantities of isomorphous bodies fill an equally large space.*

Before we proceed to the special consideration of isomorphous bodies, to learn under what limitations we must admit the validity of Mitscherlich's law, and how far the proposition of Kopp is confirmed by experience, it seems to me to be necessary, or at any rate advisable, to characterise somewhat more empirically those bodies which we name isomorphous, and at the same time investigate how far they may be distinguished in crystallization from those which are not isomorphous with them. This will be a further elucidation of the previous observations of Gay-Lussac and Beudant.

If we add chloride of sodium, or chloride of potassium, to an aqueous solution of nitrate of potash, and evaporate the solution till crystallization occurs, the nitrate of potash separates and the chloride of sodium remains in the mother-liquid. The solid mass of the crystals of nitrate of potash contains no chloride of sodium; the chloride of sodium, which is very commonly found mixed with nitrate of potash, arises partly from the mother-liquid drying on the crystals, and partly because the latter, if of considerable size, are internally hollow, and retain the mother-liquid in their cavity. By repeated crystallization the whole of the chloride of sodium may be removed, and the crystals left

perfectly pure. The same is the case with respect to a solution of carbonate of soda, to which a little sulphate of soda has been added. It yields on evaporation crystals of carbonate of soda, which contain no sulphate of soda in their solid mass, but are often rendered impure by this salt in the mother-liquid adhering to or occurring between the crystals; the latter may, however, be obtained perfectly pure by repeated crystallizations. The same thing may be observed in a solution of sulphate of copper to which persulphate of iron has been added; on evaporation it yields crystals of sulphate of copper, which can only contain a portion of the salt of iron by the adhesion of the mother-liquid, in which this salt remains. The copper salt may, by repeated crystallizations, be obtained perfectly free from the adherent iron salt.

We may easily perceive that the separation of salts by frequent crystallization, depends upon the incapacity of many salts to enter into the crystalline mass of other salts; this operation is, therefore, very frequently had recourse to in the purification of salts. The less easily soluble of two salts, or, where the solubility differs but little, the one that is present in the larger quantity, will first crystallize; and the mother-liquid, which then contains the remaining salt in excess, will, on further evaporation, yield crystals of the latter.

It is, however, quite different in other cases. Common alum, the well-known hydrated double salt of sulphate of potash and sulphate of alumina, readily separates in colourless crystals; the so-called chrome alum, an analogous hydrated double salt, composed of sulphate of potash and sulphate of the oxide of chromium, separates just as easily in decidedly violet crystals. On dissolving common alum and chrome alum together in water, the crystals of the former do not separate from those of the latter, but we obtain crystals that exhibit throughout their whole mass a mixture of common alum and chrome alum, and are of a lighter or darker violet colour in proportion as the former or the latter preponderates in the solution. Crystals of every shade of colour may thus be obtained, and no separation of the two salts can be effected by repeated crystallization. A solution of iodide of potassium, to which a little chloride of potassium has been added, does not on evapo-

ration yield crystals of pure iodide of potassium, and leave the chloride of potassium in the mother-liquid, but it gives crystals containing iodide of potassium and chloride of potassium, which are rendered impure by the adhesion or enclosure of the mother-liquid with its chloride of potassium, and we are unable to obtain by crystallization an iodide of potassium perfectly free from chloride of potassium. It has already been mentioned, that a solution of sulphate of copper mixed with persulphate of iron, will yield only crystals of sulphate of copper on evaporation, whilst the iron salt remains in the mother-liquid. If, however, instead of persulphate of iron we add sulphate of the protoxide, the two salts will not remain separate, crystals appearing which contain, throughout their whole mass, iron as well as copper. However frequently we may repeat the crystallization, we shall always obtain crystals of this kind; a separation of the iron protosalt from the copper salt cannot, therefore, be effected by recrystallization. If we change the protoxide of iron in the solution into sesquioxide of iron, as, for instance by the action of chlorine, we shall obtain by evaporation crystals of sulphate of copper, while the iron salt now remains in the mother-liquid. It is only in this manner, that by recrystallization we can remove the iron from sulphate of copper containing it.

Salts, and bodies in general, which enter jointly in this manner into a crystalline mass, and can occur together in crystals in the most different proportions, have been termed isomorphous, because the capacity of crystallizing in common is to be explained by similarity of form. Common alum crystallizes in octahedra; chrome alum appears in the same form; if both, therefore, occur in common in a fluid, particles of the one may combine in any and in alternate relations with those of the other to form a crystal. This is likewise the case with chloride of potassium and iodide of potassium; both salts are individually separated in the same form by crystallization, and from mixed solutions cubic crystals are produced, consisting of alternating particles of chloride of potassium and iodide of potassium, as both have an equal capacity for the process of crystallization.

Kopp has shown, as has been already mentioned, that on the occurrence of such a combined crystallization, equivalent quantities or weights of bodies must fill an equally, or at

least nearly equally large space. The equivalent of common alum is 5931, its specific gravity, according to Kopp, is 1·724; the equivalent volume is consequently $\frac{5931}{1{\cdot}724} = 3440$. The equivalent of chrome alum is 6246, the specific gravity is 1·848; and the equivalent volume is consequently $\frac{6246}{1{\cdot}848} = 3380$. We thus see that the two equivalent volumes are not absolutely of equal size. This cannot surprise us, as neither the equivalent weights nor the specific gravities, on which the calculation of the equivalent volumes are based, are absolutely whole numbers. Where we find a close approximation to an agreement, the want of perfect accordance may generally be ascribed to the inaccurate determination of the specific gravity. But even in differences of the equivalent volumes, which, from their greater amount, cannot be referred to the want of exactness in question, there is either a similarity, or at any rate so great a resemblance of the forms exhibited, as to show us that we are still dealing with isomorphism. If, for instance, the crystals of compounds having nearly the same equivalent volume belong to the regular system, the influence exercised by the deviation in the equivalent volume will extend, in like manner, in all dimensions, and in all three axes of the crystal, and, consequently, the form must remain wholly unchanged as the angular dimensions continue the same. But if the crystals belong to other systems, the influence spoken of will be extended in a different way upon the different axes of the crystal, a change of the angular relations taking place, and the form not, therefore, remaining absolutely the same. In this case, however, we also term the bodies isomorphous; at any rate, the suggestion made of replacing the word isomorphous by homöimorphous, (similarly formed,) has not been generally adopted.

Mitscherlich has ascertained, as already mentioned, that a like chemical constitution corresponds with the similarity of form of isomorphous bodies.

$$\text{Common alum is } \dot{\dot{K}}\dddot{S} + \ddot{A}l\,\dot{A}l\dddot{S}_3 + 24\dot{H}$$

$$\text{Chrome alum is } \dot{\dot{K}}\dddot{S} + \ddot{C}r\,\dot{C}r\dddot{S}_3 + 24\dot{H}$$

The constitution, like the form, is the same. If we consider these formulæ, we see that the chrome alum represents an alum

in which sulphate of alumina is replaced by sulphate of the oxide of chromium. As this substitution occurs without any change of form being induced, we are accustomed to consider sulphate of the oxide of chromium as isomorphous with sulphate of alumina. In these two salts, however, there is the same acid, consequently the oxide of chromium and alumina are also isomorphous with each other; or we may say that chrome alum is an alum in which the alumina is replaced by the oxide of chromium without any change of form. As now the oxide of chromium and alumina have one constituent in common, namely, oxygen, chromium and aluminum must also be isomorphous; or we may finally say, that chrome alum represents an alum in which there is chromium in the place of the aluminum of common alum. Chloride of potassium and iodide of potassium are isomorphous, both containing the same metal, potassium; consequently, chlorine and iodine are isomorphous.

In accordance with the view, that isomorphous combinations proceed from the union of isomorphous constituents, which, as may easily be perceived, leads us to the groups of isomorphous elements, we define isomorphous bodies as those which may replace each other in chemical combinations, of course where the weights are equivalent, without any change of form being induced. We say that the oxide of chromium may replace alumina, in combination, without a change of form, protoxide of iron may replace protoxide of manganese, chromium may replace aluminum, and iron may replace manganese. The formulæ which are applied to combinations in which isomorphous bodies occur, correspond with this view, which, as we shall see below, is not perhaps throughout correct.

The following is the formula for that spathic iron, which, besides protoxide of iron, also contains protoxide of manganese and magnesia.

$$\left.\begin{matrix}\dot{\mathrm{Fe}}\\ \dot{\mathrm{Mn}}\\ \dot{\mathrm{Mg}}\end{matrix}\right\}\ddot{\mathrm{C}}.$$

This formula does not designate a combination of 1 equiv. of carbonic acid, 1 equiv. of protoxide of iron, 1 equiv. of protoxide of manganese, and 1 equiv. of magnesia, but a combination in which there is added to 1 equiv. of carbonic acid 1 equiv.

made up of protoxide of iron, protoxide of manganese, and magnesia together. The amount of oxygen contained in these three different bases is, when taken together, 1 equiv., and we should therefore, perhaps, be more correct if we were to write $\left\{\begin{matrix}\dot{\mathrm{Fe}}\\ \mathrm{Mn}\\ \mathrm{Mg}\end{matrix}\right\}\ddot{\mathrm{C}}$.

The formula for the mixt alum composed of alumina alum and chrome alum would, according to this, be as follows:—

$$\dot{\mathrm{K}}\,\dddot{\mathrm{S}}\left\{\begin{matrix}\ddot{\mathrm{Al}}\,\dot{\mathrm{Al}}\\ \mathrm{Cr}\,\mathrm{Cr}\end{matrix}\right\}\dddot{\mathrm{S}}_3 + 24\dot{\mathrm{H}},\ \&c.$$

As the upright bracket occupies a considerable amount of room in printing, it would be better perhaps to place the symbols of isomorphous bodies alongside, instead of above one another, in order to be able to connect them by means of a horizontal bracket, as for instance, thus:

$$\overbrace{\mathrm{Fe}\,\mathrm{Mn}\,\mathrm{Mg}}^{\cdot}\,\ddot{\mathrm{C}};\quad \dot{\mathrm{K}}\,\dddot{\mathrm{S}},\ \overbrace{\mathrm{Al}\,\mathrm{Al}\,\mathrm{Cr}\,\mathrm{Cr}}^{\cdots}\,\dddot{\mathrm{S}}_3 + 24\dot{\mathrm{H}}.$$

I wonder that those critics, who suffer nothing to escape their attacks, have not animadverted upon the customary mode of writing the formula for the combinations in which isomorphous bodies are contained. They might possibly maintain that these formulæ are quite unwarrantable, especially where the word atom is used for equivalent. We designate by the formula $\mathrm{Fe\,O,\ C\,O_2}$, a combination which we suppose consists of 1 at. of protoxide of iron and 1 at. of carbonic acid; the formula $\left\{\begin{matrix}\mathrm{Fe\,O}\\ \mathrm{Mn\,O}\\ \mathrm{Mg\,O}\end{matrix}\right\}\mathrm{C\,O_2}$ designates, according to the strict meaning, a combination of 1 at. of carbonic acid with alternating fractions of 1 at. of protoxide of iron, protoxide of manganese and magnesia, which is evidently at variance with the indivisibility of atoms.

It is, however, clear that this formula is only an abbreviation of $\left\{\begin{matrix}m\mathrm{Fe\ O,\ C\,O_2}\\ n\mathrm{Mn\ O,\ C\,O_2}\\ o\mathrm{Mg\ O,\ C\,O_2}\end{matrix}\right.$ in which m, n, and o are alternating quantities of weights. The above-mentioned spathic iron

has been formed from a fluid, in which the three isomorphous salts, carbonate of protoxide of iron, carbonate of protoxide of manganese, and carbonate of magnesia, are contained, and crystals are thus formed, in which alternating and various quantities of the individual salts enter into combination. If we suppose 1000 atoms of the above-named carbonate in an individual crystal of spathic iron, 700 at. may be carbonate of protoxide of iron, 200 at. carbonate of protoxide of manganese, and 100 at. carbonate of magnesia; but at the same time every other kind of relation may occur. On this account, therefore, as already mentioned, we shall most correctly define isomorphous bodies to be such as, in consequence of a like constitution, and on account of like equivalent volumes, possess like crystalline forms, and may also crystallize in common in the same form. If we assume the numbers to be large enough, we shall be able to reckon how many equivalents of the one isomorphous salt and how many of the other occur in a mixed combination. If the relation be a simple one it is customary to express it in the formula. The magnesian spar of Zillerthal, Jena, and some places, has the following formula $\left\{\begin{matrix}\frac{1}{2}\dot{\mathrm{Ca}}\\ \frac{1}{2}\dot{\mathrm{Mg}}\end{matrix}\right.\ddot{\mathrm{C}}$ or $\overbrace{\frac{1}{2}\mathrm{Ca}\,\frac{1}{2}\mathrm{Mg}}\,\ddot{\mathrm{C}}$, which is intended to show that this combination is not to be regarded as $\dot{\mathrm{Ca}}\,\ddot{\mathrm{C}}+\dot{\mathrm{Mg}}\,\ddot{\mathrm{C}}$, that is to say, as a double salt of carbonate of lime and carbonate of magnesia, but as a mixture of isomorphous salts in the relation indicated. In the same manner, the magnesian spar of Halle in the Tyrol, of Saberg, and many other places where it is found, has the formula $\overbrace{\frac{1}{4}\mathrm{Ca}\,\frac{3}{4}\mathrm{Mg}}\,\ddot{\mathrm{C}}$, containing 3 at. of carbonate of magnesia to 1 at. of carbonate of lime.

We shall now turn to the special consideration of the most important and interesting isomorphous groups, in which an opportunity will often occur of specially developing what has already been given in general outline.

Titanic acid and binoxide of tin are isomorphous, for the former crystallizes as rutile, the latter as tin-stone, in the

same forms of the Second System of crystallization*. The binoxide of tin is $Sn O_2$, titanic acid $Ti O_2$, and, according to Kopp, both combinations have the same equivalent volume, (*Annal. der Chem. und Pharm.*, Bd. 36, s. 5;) the isomorphism is, therefore, founded here upon like number and grouping of the atoms (Mitscherlich's law), and upon like size of the chemical atoms of the compounds (Kopp's law). As may be seen by consulting the tables of the equivalent volumes (atom-volumes) of the elements, titanium and tin have not the same equivalent volume in a free condition, for that of titanium is 56, while that of tin is 101; it is, therefore, impossible for 56 c. c. of titanium to replace 101 c. c. of tin without a change of form occurring, and hence tin and titanium cannot possibly be isomorphous in an isolated condition, and hence it follows, consequently, that isomorphism of the constituents is not to be inferred, or, at any rate, not absolutely, from the isomorphism of analogous combinations,—or that the isomorphism of combinations is either not at all, or not always, based upon the isomorphism of the constituents. The isomorphism of binoxide

* The Systems of Crystallization will be referred to by their numbers, which, with their synonymes, are as follows:—

1. The First System, or Regular System, characterized by three axes which are similar and at right angles to each other. The regular system of Weiss. The octahedral system of Miller.

2. The Second System, characterized by three perpendicular axes, but of which two only are similar. The two-and-one-axis system (4-membered) of Weiss. The pyramidal system of Miller.

3. The Third System, characterized by *four* axes, of which three similar are placed in the same plane and cut each other at angles of 60°; the fourth axis is different, and stands perpendicular to the plane of the other three. The three-and-one-axis system (6-membered) of Weiss. The rhombohedral system of Miller.

4. The Fourth System, characterized by three axes which are unlike, but perpendicular to each other other. The one-and-one-axis system (2-and-2-membered) of Weiss. The prismatic system of Miller.

5. The Fifth System, characterized by three unlike axes; two of which are oblique to each other, but the third is perpendicular to the plane of the other two. The two-and-one-membered system of Weiss. The oblique prismatic system of Miller.

5. The Sixth System, characterized by three unlike axes which are all oblique to each other. The one-and-one-membered system of Weiss. The doubly oblique prismatic system of Miller. (See the *Principles of Crystallography*, by V. Regnault.)—Ed.

of tin and titanic acid can, therefore, only occur where, in one or other of the two combinations, either the oxygen or the metal is contained with some other than the original equivalent volume.

According to the table (page 14), titanic acid contains oxygen with the equivalent volume 32, whilst the binoxide of tin contains oxygen with the equivalent volume 16, if we assume the metal to be contained in it with its original equivalent volume. The equivalent volume of titanium is expanded $1\frac{1}{2}$ times in titanic acid, if, as in the case of binoxide of tin, we assume the oxygen to be contained with the equivalent volume 16.

Alumina (corundum), sesquioxide of iron (ologistic iron), and oxide of chromium, are isomorphous; they crystallize in the Third System. The composition of these oxides is perfectly analogous, corresponding to the formula $R_2 O_3$; their equivalent volumes are of equal size (Kopp, page 5), or only present such differences as may be explained on the want of perfect identity of form. For instance, the same angle measures 85° 58′ in ologistic iron, and 86° 6′ in corundum. (See above, and also further on.) Here, too, the isomorphism of the combinations is not based upon the isomorphism of the constituents, for the equivalent volume of iron is 45, while that of chromium is 64, (page 4;) the isomorphism is therefore dependent upon the oxygen entering into sesquioxide of iron with the equivalent volume 32, and into oxide of chromium with that of 16; the equivalent volume of sesquioxide of iron is, therefore, $2\times45+3\times32=186$, that of oxide of chromium is $2\times64+3\times16=176$. With ologistic iron, ilmenite (titanic iron) is isomorphous. According to Mosander, the latter may be considered as a titanate of the protoxide of iron ($Fe O$, $Ti O_2$); whence sesquioxide of iron and titanate of protoxide of iron, although two combinations of totally different constitution, but of like number of atoms, are isomorphous, and we might conclude that isomorphism requires no similarity of constitution, but only equality in the number of the atoms. Ilmenite may, however, also be regarded as sesquioxide of iron, in which 1 equivalent of iron is replaced by 1 equivalent of titanium. If, then, we write the formula for sesquioxide of iron as $Fe+Fe+3O$, and that for ilmenite as $Fe+Ti+3O$,

the isomorphism is based upon similarity of constitution*. The equivalent volume of ilmenite is likewise nearly equal to that of sesquioxide of iron. In the same manner, however, as the equivalent volume of chromium deviates from that of iron, so also does that of titanium; for that of iron is 45, and that of titanium 56, and consequently titanium and iron are as little isomorphous in an isolated condition as chromium and iron. The equivalent volume of sesquioxide of iron is, as stated above, 186, that of the combination, $Fe\,Ti\,O_3$, amounts, in like manner, to $45+56+96=197$, consequently so nearly equal to that of sesquioxide of iron that isomorphism may occur.

Kopp is of opinion that bodies which are not themselves isomorphous with others, may together yield isomorphous combinations, without any change occurring in their equivalent volume; that is, when they form the preponderating quantity, and where the deviation of the equivalent volume does not exercise any disturbing influence upon the isomorphism.

Oxide of antimony, $Sb\,O_3$, and arsenious acid, $As\,O_3$, which, are dimorphous, being both capable of crystallising in the First and Fourth Systems, are isomorphous in both forms. The isomorphism of these two combinations has long remained undetected, owing to their dimorphism, notwithstanding that it was conjectured from the similarity of their composition and of their chemical relation. Previous to their dimorphism being discovered, there was only the regular form known for arsenious acid, while, in the case of the oxide of antimony, the form of the Fourth system was known, contrary to what was the case with the arsenious acid, and thus it was naturally believed that arsenious acid crystallized in the First System, and that oxide of antimony, which is so similar to the former in chemical relations, crystallized quite differently, namely, in the Fourth System. Their dimorphism has led to the discovery of their isomorphism. The equivalent volume of the two combinations is equally large, that of the oxide of antimony, is, for instance, $\frac{1913}{5\cdot56}=344$, that of arsenious acid $\frac{1237\cdot5}{3\cdot7}=334$; the equi-

* A sesquioxide of titanium, Ti_2O_3, has lately been formed, which establishes a different conclusion, that ilmenite is a *mixture* of two isomorphous oxides, Ti_2O_3 and Fe_2O_3.—Ed.

valent volume of antimony is, however, 240, that of arsenic is 160, so that the two metals cannot be isomorphous in an isolated condition, provided dimorphism, and different allotropic conditions with which we are as yet unacquainted, do not occur.

It is worthy of remark that the equivalent volume of antimony is exactly $1\frac{1}{2}$ times that of arsenic.

If, therefore, we suppose the antimony to be contained in the oxide of antimony, and the oxygen, with the respective equivalent volumes of 240 and 32 without condensation or expansion (page 14), we may assume that the arsenic is contained in the arsenious acid with $1\frac{1}{2}$ times its original equivalent volume.

As arsenious acid and the oxide of antimony, so the corresponding sulphur compounds of arsenic and antimony, orpiment, $As\,S_3$, and common antimony ore, $Sb\,S_3$, are likewise isomorphous, as both occur in forms of the Fourth System. The equivalent volume of both is equally great. The combinations of both sulphides with sulphide of silver, the light red silver ore, $3Ag\,S + As\,S_3$, and the dark red silver ore, $3Ag\,S + Sb\,S_3$, crystallize in the same rhombohedra; in like manner, arsenic-fahlerze and antimony-fahlerze are isomorphous, and have the same equivalent volume.

Arsenide of nickel (Kupfer-nickel), $Ni_2\,As$, and antimonide of nickel, $Ni_2\,Sb$, two combinations in which arsenic and antimony are to be regarded as negative constituents, are likewise isomorphous in forms of the Third System. Sulphide of nickel (Haarkies), $Ni\,S$, or $Ni_2\,S_2$, has the same form as these, a combination of different chemical constitution, and consisting of 2 equivalents of nickel and 2 equiv. of sulphur. Whilst arsenide and antimonide of nickel contain 1 equiv. of arsenic and antimony to 2 equiv. of nickel. We shall become acquainted with other examples, in which similarity of form occurs with great difference of the generally assumed chemical constitution. Here we must either recognise an isomorphism without reference to similarity of form, or we must grant that the law of Mitscherlich is not generally applicable, or we must finally endeavour to harmonise the constitution with this law. If we hold to the

equivalents of arsenic, antimony, and sulphur, and speak of isomorphism between arsenide, antimonide, and sulphide of nickel, we must assume that 2 equiv. of sulphur in the sulphide of nickel are isomorphous with 1 equiv. of antimony and arsenic in the antimonide of nickel, and arsenide of nickel. If, however, we divide the equivalent of arsenic and antimony into two atoms, as the specific heat of these metals demands, and as the volume-theory requires according to Berzelius, we obtain for arsenide of nickel and antimonide of nickel the formulæ Ni As and Ni Sb, which perfectly correspond with the formula for sulphide of nickel, Ni S. A division of the equivalents of arsenic and antimony into two atoms may indeed be based upon the isomorphism of arsenide of nickel, antimonide of nickel, and sulphide of nickel.

If we compute the equivalent volumes of the three combinations according to this last formula, we find that arsenide of nickel and sulphide of nickel have nearly the same equivalent volume, but that the equivalent volume of arsenide of nickel is nearly $1\frac{1}{2}$ times greater. Kopp's law, consequently, does not allow of the isomorphism of the three combinations.

Iron pyrites, $Fe\,S_2$, and arsenical or speiss-cobalt, Co As, crystallize in the same hemiedric forms of the First System, and what has already been said applies also to these, for iron and cobalt have the same equivalent volume, and are, therefore, certainly isomorphous. We must, consequently, either assume that S_2 is isomorphous with As, or change the formula Co As into $Co\,As_2$, in order to establish the similarity of constitution. Here, too, isomorphism cannot be explained by similarity of the equivalent volumes, for the equivalent volume of cobalt blende is almost exactly $1\frac{1}{2}$ times greater than that of iron pyrites. A similar form to that of the above-named compounds is presented by cobalt blende, $Co\,S_2 + Co\,As_2$, nickel blende, $Ni\,S_2 + Ni\,As_2$, and even by nickel-antimony blende, $Ni\,S_2 + Ni\,Sb_2$. Cobalt blende and nickel blende have the same equivalent volume; the equivalent volume of the nickel-antimony blende is, however, only about $\frac{2}{3}$ as large, namely, the same as that of speiss-cobalt. This is, as has been stated, $Co\,As_2$; if, therefore, we write the formula for nickel-antimony

blende thus, $\overbrace{Ni\,\frac{1}{2}S_2\,\frac{1}{2}Sb_2}$, both have a like form, a like equivalent volume, and a like constitution. As cobalt blende, $Co\,S_2 + Co\,As_2$, is isomorphous with sulphide of iron, $Fe\,S_2$, occurring as pyrites, we might assume that arsenical pyrites, $Fe\,S_2 + Fe\,As_2$, would be isomorphous with cobalt blende. Such, however, is not the case, but arsenical pyrites is isomorphous with that second form of the bisulphide of iron, with white pyrites (Sperkies,) having an equivalent volume approximating to that of the latter. (See Rammelsberg, *Lehrbuch der Stöchiometrie*, page 241.)

Sulphide of lead, Pb S, and selenide of lead, Pb Se, are isomorphous, crystallizing in forms of the First System. With the same constitution they have also the same equivalent volume. It is probable that sulphur and selenium have also the same equivalent volume in an isolated condition, for as selenium can only with great difficulty be obtained free from porosities, the specific gravity is probably found somewhat too low. The same, perhaps, holds good for tellurium, which, in a chemical point of view, stands together with sulphur and selenium.

Many other metallic sulphides, composed according to the formula R S, appear in forms of the regular system, as, for instance, sulphide of zinc, Zn S, zinc blende and sulphide of silver, Ag S. Does isomorphism occur here amongst themselves and with sulphide of lead? The form is the same, and the constitution we also assume to be the same, why, therefore, should we not call it isomorphism? The equivalent volume of the sulphide of silver is nearly the same as that of sulphide of lead, that of sulphide of zinc differs considerably from both, but this difference of the equivalent volume does not exercise the same influence upon crystals appertaining to the regular systems, as to those belonging to the other systems. On the other hand, we must observe that lead, silver, and zinc are not approximated by any other cases of isomorphism, and that even if silver and lead show some resemblance in a chemical character, zinc differs very much from them in this respect. We have already mentioned that the substitution in different crystals for each other is a main characteristic of isomorphous

bodies, but I am not aware that sulphide of zinc and sulphide of lead, or sulphide of zinc and sulphide of silver, can enter indifferently into the same crystal. It is likewise uncertain whether the silver obtained from galena exists as sulphide of silver in the mass of its crystals, or whether it originates from other commingled combinations containing sulphide of silver. We must also observe here, that the occurrence of forms appertaining to the regular system is not sufficient to establish isomorphism, since bodies, which are evidently of different composition, and of which there can be no idea of isomorphism—if we do not adhere to the mere verbal meaning of the term—occur in such forms; chloride of sodium crystallizes, like galena, in cubes; diamond, magnetic iron, and alum crystallize in octahedrons, phosphorus and garnet in the garnet dodekahedron.

Even in other systems, although more rarely, we meet with the same form combined with a very decidedly different constitution, so that even here, with identity of form, we must not speak of isomorphism without some limitation.

The natural disulphide of copper, Cu_2S, (copper blende) crystallizes in a form of the Fourth System. On its being fused, or on fusing large masses of copper and sulphur, we obtain octahedral, consequently regular crystals of disulphide of copper. (G. Rose, Mitscherlich.) Disulphide of copper, Cu_2S, is consequently dimorphous. As the natural sulphide of silver, AgS, likewise occurs in forms of the regular system, and as, according to Becquerel, artificial sulphide of silver is also obtained in octahedrons, we may say that Cu_2S and AgS are isomorphous. The circumstance that silver and copper blende combined, $Cu_2S + AgS$, occurs in the form of copper blende, is in favour of the isomorphism of both sulphides.

It is, however, most certainly proved, according to H. Rose, that Cu_2S and AgS replace each other in alternating relations in Polybasite. We must now either admit that under some circumstances Cu_2 is isomorphous with Ag in combination, or we must divide the equivalent of silver into 2 atoms, as is required by the specific heat of the silver. If we carry out this division, copper blende and silver blende will have a

like atomic constitution, the former is $Cu_2 S$, the latter $Ag_2 S$. The equivalent volumes of both combinations differ very much in other respects from each other. We shall subsequently see what are the results from the division of the equivalent of silver into 2 atoms.

Isomorphism may be best observed in salts, owing to their peculiar tendency to form crystals. We shall very much facilitate our view of combinations in these classes if we place together those cases of isomorphism in which the halogen (salt-radical), or the acid is different, and then those in which the metal or the base are different.

The salts of tungstic acid are isomorphous with the analogous molybdates. Thus, molybdate of lead (yellow lead earth) and tungstate of lead occur in similar forms of the Second System. The constitution of these salts is the same, for instance, the formula of tungstic acid is $Wo O_3$, that of molybdic acid $Mo O_3$.

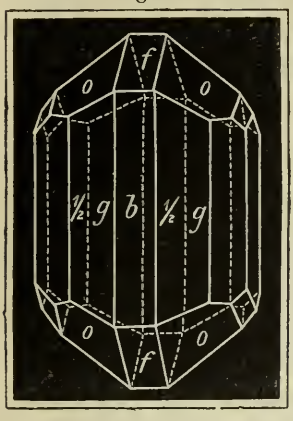
Sulphates, seleniates, chromates, and manganates of the same base, form well-marked groups of isomorphous salts. The analogous salts of these acids, which all contain 3 atoms of oxygen to 1 atom of the positive constituent, are isomorphous, when free from water, or when they contain an equal number of atoms of water of crystallization. Thus, neutral sulphate of potash and chromate of potash, which are both anhydrous, crystallize in the same form of the Fourth System.

The same applies to anhydrous and hydrated sulphate and seleniate of soda, and to anhydrous sulphate and seleniate of silver. The acid sulphate of potash ($K O, S O_3 + H O, S O_3$) has the same form as the corresponding seleniate. Isomorphism extends also to the double salts; thus, for instance, the ammoniacal sulphate, seleniate, and chromate of silver, have the same form. ($Ag O, S O_3 + 2 N H_3$, &c.)

The equivalent volume of sulphate of potash is $\frac{1089}{2 \cdot 66} = 409$, the equivalent volume of chromate of potash is $\frac{1217}{2 \cdot 7} = 451$; the two salts have therefore only an approximatively equal equivalent volume. As the angular relations of their crystals are not exactly equal but merely approximatively so, the salts, strictly speaking, are not isomorphous, but homœmor-

phous. Fig. 1 exhibits a prism frequently met with in these salts. According to Mitscherlich (*Pogg. Annal.*, Bd. 18, s. 168), the inclination of two of its faces is as follows:

Fig. 1.



In sulphate of potash	$\frac{1}{2}$ g : $\frac{1}{2}$ g	112° 22′
„ chromate „	$\frac{1}{2}$ g : $\frac{1}{2}$ g	111° 10′

so that the greater equivalent volume corresponds to the smaller angle of inclination. In seleniate of potash this angle amounts to 111° 48′ 5″, in sulphate of ammonia to 111° 15′.

Johnston has observed that chromate of lead is dimorphous, and isomorphous in its least frequent forms with molybdate of lead. This establishes an affinity between molybdic, chromic, sulphuric, and other analogous acids.

The salts of phosphoric and arsenic acids constitute another well defined isomorphous group. For every arseniate there is a phosphate, corresponding, with respect to its composition, with the former, and having the same form. Thus, ordinary arseniate and phosphate of soda exhibit a like crystalline form, and have also a similar composition (Graham's *Chemistry*); each of the salts contains 2 equivalents of soda and 1 equiv. of water as bases, with 1 equiv. of acid and 24 equiv. of water of crystallization. With a different quantity of water of crystallization, namely, with 14 equiv., the form of this salt is quite different, but it is again the same in both. The so-called acid salts of these acids, which, for 1 equiv. of soda and 2 equiv. of water as bases, contain 1 eq. of acid and 2 of water of crystallization, have the same form. Phosphate and arseniate of lead, which are likewise isomorphous, replace each other in alternating and undetermined relations in the native arseniates and phosphates of lead.

We do not know whether phosphoric and arsenic acids are themselves isomorphous; both are known as anhydrous in an amorphous condition only. Phosphorus and arsenic, however, are not isomorphous; the former crystallizes regularly, the latter according to the Third System, and the equivalent volumes are different. It is possible, however, that the isomorphism

here is concealed by dimorphism, and that the phosphorus possesses a different form in different allotropic conditions. Chlorine, bromine, and iodine have the same equivalent volume, and their analogous combinations are isomorphous. Thus the chlorides are isomorphous with the iodides and bromides, the chlorides with the iodates and bromates, and the perchlorates with the periodates. All these combinations correspond exactly with respect to their composition. Iodic acid and bromic acid contain, like chloric acid, 5 equiv. of oxygen to 1 equiv. of the halogen; periodic acid contains, like perchloric acid, 7 equiv. of oxygen to 1 equiv. of halogen. Cyanogen and fluorine appear also to belong to this group; cyanogen has the same equivalent volume as chlorine, &c. (p. 4.) The cyanides and fluorides have the same form as the chlorides, and in the case of chloride and fluoride of calcium replace each other in alternating relations: $\left.\begin{matrix}\mathrm{Ca\,F}\\ \mathrm{Ca\,Cl}\end{matrix}\right\} + 3\,\mathrm{Ca\,O},\ \mathrm{P\,O_5}$. The permanganates are isomorphous with the perchlorates; thus permanganate of potash and perchlorate of potash may be substituted for each other in crystals like other isomorphous bodies. Perchloric acid, however, contains 1 equiv. of chlorine to 7 equiv. of oxygen, whilst 2 equiv. of manganese occur together with 7 equiv. of oxygen in permanganic acid, and we must therefore assume, that 2 equiv. of manganese can replace 1 equiv. of chlorine, without producing any change of form, or, as we are accustomed to say, that 2 equiv. of manganese in the permanganates are isomorphous with 1 equiv. of chlorine in the perchlorates. The isomorphism of the perchlorate and permanganate of potash is regarded by Berzelius as the most decided reason for the division into two parts of the equivalent of chlorine, and consequently also of bromine, iodine, &c., a division which, as we know, is also required by the volume theory, and which corresponds best with the specific heat of chlorine. Berzelius expresses himself decidedly, that it is undoubted that permanganic acid consists of 2 atoms of manganese and 7 atoms of oxygen: as now perchlorate of potash is isomorphous with permanganate of potash, it follows that perchloric acid must consist of 2 atoms of chlorine and 7 atoms of oxygen analogous to permanganic acid. In the same manner hypochlorous acid

consists of 2 atoms of the radical and 1 atom of oxygen. Hence it further follows, continues Berzelius, that if hypochlorous acid be formed of 2 vols. of chlorine gas and 1 vol. of oxygen gas, these two gases must, with the same volume, contain an equal number of atoms; while he further derives the division of the hydrogen equivalents into 2 atoms from the substitution of hydrogen by means of chlorine, volume for volume, in organic combinations.

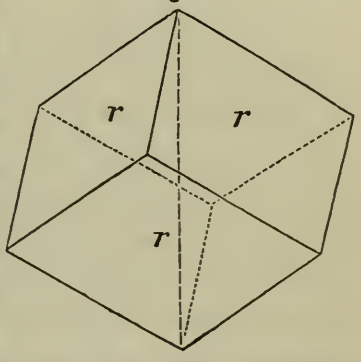
If we divide the equivalent of chlorine into 2 atoms, we can explain the isomorphism existing between perchlorate of potash and permanganate of potash, by the similarity of the chemical constitution of the salts, that is, by their consisting of an equal number of similarly grouped atoms, corresponding to the law established by Mitscherlich ($KO, Mn_2 O_7$ and $KO, {}^{v}Cl_2 O_7$.) We have, however, already seen many cases, and will have occasion to observe many more, to which this law cannot be applied in its full force. I fully admit the value which isomorphism has for the determination of constitution within certain groups of combinations, but if we are to admit that 1 atom of silver in sulphide of silver (Ag S) has the same value in an isomophous relation as 2 atoms of copper in disulphide of copper (Cu_2 S), when we see that 1 atom of magnesia, protoxide of iron, &c., may be replaced without any change of form by 3 atoms of water, (see further on,) and that ammonium, a group of 5 equivalents (H_4 N), may take the place of 1 equivalent of potassium, it is not difficult to assume, that 2 atoms of manganese and 1 atom of chlorine may mutually replace each other in the above-named combination without any change in form. Berzelius, in the last edition of his Manual, has set down the atomic weight of ammonium as equal to its equivalent weight (${}^{v}H_8 {}^{v}N_2$), whilst previously the equivalent of ammonium was made to consist of 2 atoms (${}^{v}H_4 {}^{v}N$). It would certainly be very striking to halve the equivalent of chlorine on account of its isomorphous relations, and not carry out this division in the equivalent of potassium, which is as urgently demanded, if 1 atom of ammonium be set down as $=$ ${}^{v}H_4 {}^{v}N$. It may further be urged against the division of the equivalent of chlorine into 2 atoms, that dichloride of copper (Cu_2 Cl) is isomorphous with dinoxide of copper (Cu_2 O), but as both combinations

occur in forms appertaining to the regular system, we lay little stress upon this isomorphism.

Isomorphous groups of salts, whose acids are the same, but their bases different, are still more frequent than the above-enumerated isomorphous groups of salts, with like base and different acids. A very remarkable group of this kind is formed by those carbonates which are comprised in mineralogy under the name of spars:—

Calc-spar.... .... $Ca\,O, Co_2$	Iron-spar.... .... $Fe\,O, C\,O_2$
Dolomite.... .... $\left.\begin{matrix}\frac{1}{2}Mg\,O\\ \frac{1}{2}Ca\,O\end{matrix}\right\} Co_2$	Talc-spar.... .... $Mg\,O, C\,O_2$
Manganese-spar $Mn\,O, Co_2$	Zinc-spar .... $Zn\,O, C\,O_2$

Fig. 2.



The fundamental form of all these salts is a rhomboid, (fig. 2,) and their bases replace each other in the most various relations in the crystals. Thus spathic iron almost always contains carbonate of protoxide of manganese and carbonate of magnesia; manganese spar contains carbonate of the protoxide of iron, carbonate of magnesia, and carbonate of lime; the zinc spar, carbonate of the protoxide of iron, &c. As, however, a perfectly exact agreement of form does not occur in sulphate, chromate, and seleniate of potash, so there are likewise differences that deserve notice, with regard to the angular relations of the principal rhomboid in these different salts; the angle of inclination at the extreme edges of this rhomboid varying from 105° 5′ to 107° 40′. The following table shows that this difference of form stands in the closest connection with the difference of the equivalent volume:—

Formula.		Equiv.	Spec. Grav.	Equiv. Vol.	
$\dot{Ca}\,\ddot{\dot{C}}$	....	625	2·72	230	105° 5′
$\left.\begin{matrix}\frac{1}{2}\dot{Ca}\\ \frac{1}{2}\dot{Mg}\end{matrix}\right\}\ddot{\dot{C}}$	....	579	2·88	201	106° 15′
$\dot{Mn}\,\ddot{\dot{C}}$	....	720	3·59	200	106° 51′
$\dot{Fe}\,\ddot{\dot{C}}$	....	625	3·83	189	107° 0′
$\dot{Mg}\,\ddot{\dot{C}}$	....	533	3·00	178	107° 25′
$\dot{Zn}\,\ddot{\dot{C}}$	....	781	4·44	176	107° 40′

We see that the size of the equivalent volume corresponds to the smallness of the solid angle. Kopp has given a formula for this relation of the equivalent volumes to the solid angle, (*Annal. der Chemie und Pharm.*, Bd. 36, s. 15,) and Rammelsberg draws attention to the fact, that in dolomite, which may be looked upon as a combination of $\frac{1}{2}$ an equivalent of carbonate of lime, (calc-spar,) and $\frac{1}{2}$ an equivalent of carbonate of magnesia (talc-spar), and its equivalent volume, therefore, the arithmetical mean of the equivalent volumes of these two constituents, the size of the angle in question is also the exact arithmetical mean of their size in calc-spar and talc-spar, namely, $\frac{105° 5' + 107° 25'}{2} = 106° 15'$.

If the diminution of the angle of the terminal edges of the rhombohedron be really dependent upon the augmentation of the equivalent volume, this angle will not only become smaller, if one constituent is replaced in the crystals by another of larger equivalent volume, as, for instance, carbonate of magnesia by carbonate of lime, but it will also become smaller if an increase of the equivalent volume be produced by any other means. This may happen by the crystals being heated, since by the action of heat the density is diminished, and the equivalent volume is increased. Mitscherlich has long since shown that heat exercised the influence in question upon the angle of this crystal. Crystals belonging to the regular system are equally expanded in all dimensions, the angular relations remain, therefore, the same, notwithstanding that the equivalent volume is increased in size. The same must, consequently, also be the case when, in crystals of this kind, constituents which are not of absolutely equal equivalent volume replace each other.

The salts of baryta, strontia, and lead of the same acids form well-marked isomorphous groups. Sulphate of baryta (heavy spar), sulphate of strontia (celestine), sulphate of lead, crystallize in the same form of the Fourth System. Carbonate of baryta (witherite), carbonate of strontia (strontianite), and carbonate of lead (white lead ore), have likewise the same crystalline form, belonging also to the Fourth System, but differing in each. The anhydrous nitrates of

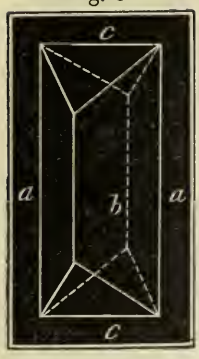
these bases, and the bromates with 1 equiv. of water, are likewise isomorphous.

The group of the carbonates of these bases is allied, in an interesting manner, with the preceding group, namely by dimorphism of some of the members. Carbonate of lime, as arragonite, has, for instance, exactly the same form as the carbonates of baryta, strontia, and lead, and is, consequently, isomorphous with them; on this account we often find a portion of the lime replaced in arragonite by strontia, or even by oxide of lead. On the other hand, it appears that carbonate of lead can occur in the other form of carbonate of lime, as calc-spar, and consequently that it may also be dimorphous, for we find in plumbocalcite, which has the form of calc-spar, carbonate of lead in alternating relations with carbonate of lime. We should never, therefore, have suspected the isomorphism of these two carbonates, had we only learnt to know them in their ordinary forms. This is a highly important fact, for the deficiency of isomorphism between other bodies may also be occasioned by their being dimorphous, when the two forms have not yet been fully ascertained. According to Dufrénoy, the form possessed by carbonate of protoxide of iron as junkerite is also that of arragonite; this salt is therefore likewise dimorphous.

Lime is connected with oxide of lead, baryta, and strontia, by the salts of other acids. Thus, apatite, $Ca\,Cl + 3Ca\,O, P\,O_5$, and native phosphate of lead, $Pb\,Cl + 3Pb\,O, P\,O_5$, have the same crystalline form; and in the latter, a portion of the phosphate of lead is often replaced by phosphate of lime, as also occasionally a part of the chloride of lead by fluoride of calcium. It has already been mentioned that arsenic acid occurs in the place of phosphoric acid. The hyposulphates of strontia, oxide of lead and lime, crystallize with 4 equiv. of water, according to the Third System, and are likewise isomorphous among themselves. (Heeren.)

What has been said of the relation existing between form and equivalent volume in the groups of spars, also applies to the groups of salts of baryta, strontia, and lead, and to those salts of lime which are thus isomorphous by dimorphism. The simplest characteristic form, to which the other forms may

Fig. 3.



be referred, is in the case of the carbonates of baryta, strontia, oxide of lead and lime, such as we have represented in fig. 3.

The angles of the crystals are not, however, exactly the same in these four salts; the solid angles *a* and *b*, and the angle of the ends, *c c*, are different in these, and the equivalent volumes are also different, as the following table will show.

Formula.	Equiv.	Spec. Grav.	Equiv. Vol.	Angles.		
				a	*b*	*c*
$\dot{Ba}\,\ddot{C}$....	 1230	4·30	286	118° 30′	61° 30′	106° 50′
$\dot{Sr}\,\ddot{C}$....	 921	3·60	256	117° 16′	62° 44′	108° 12′
$\dot{Pb}\,\ddot{C}$....	 1669	6·47	258	117° 14′	62° 46′	108° 13′
$\dot{Ca}\,\ddot{C}$....	 625	2·93	213	116° 16′	63° 44′	108° 27′

We here clearly perceive how the equivalent volumes most accurately agree in the salts which are most perfectly isomorphous. The differences in the angles and in the equivalent volumes are really so small in carbonate of strontian (strontianite) and carbonate of lead (white lead ore) that they may be esteemed mere errors of observation. Carbonate of baryta (witherite) and carbonate of lime, as arragonite, differ considerably from these two salts with respect to their equivalent volumes and angular relations; and an increase of the equivalent volume corresponds to an increased angle *a*, and smaller angles *b* and *c*. If we increase the equivalent volume of one of these salts, (if we heat it,) a change in the angle corresponding to this increase of the equivalent volume occurs, the angle *a* becomes more obtuse, and the angles *b* and *c* become less so. (Kopp.)

In sulphate of lead the angle *a* amounts to 101° 32′, in sulphate of baryta (heavy spar) to 101° 42′, and in sulphate of strontian (celestine) 104° 48′; here, therefore, there is no perfect isomorphism.

Interesting results present themselves when we seek to refer the isomorphism of the salts of baryta, strontia, and lead, to the isomorphism of the oxides or of the metals. If we allow the specific gravities 4·73 and 3·93, as given by Karsten, to

stand for baryta and strontia, these oxides will not have the same equivalent volume, for that of baryta amounts to 202, and that of strontia to 164; they cannot, therefore, replace each other in salts without a change of form, as like volume is necessary. But the metals of these oxides, barium and strontium, have apparently, according to Kopp, the same equivalent volume, and we might hence conclude, that in the salts of baryta and strontia, those earths and the acids are not proximate constituents, but, as the binary theory of the salts demands, barium and strontium with a compound radical; and consequently it would be more correct to write $Ba\,S\,O_4$ than $Ba\,O,\,S\,O_3$. The conversion of the one salt into the other is not then effected by an exchange of baryta and strontia, but of barium and strontium. If we include lead in this consideration, we find that its equivalent volume does not agree with those of barium and strontium, whilst the equivalent volume of oxide of lead approaches very nearly to that of strontia, being 156. With respect to salts of lead, we must therefore give the preference to the generally prevalent view of the constitution of salts, whilst we assume two different constitutions for the salts of strontia. (Kopp, *Annalen der Chemie u. Phar.* Bd. 36, s. 18.) Similar results are yielded with respect to the bases and metals of other salts, and it likewise is worthy of notice, that although chloride of barium and chloride of strontium have the same equivalent volume, that of chloride of lead differs from both.

Potash (K O) and oxide of ammonium (Am O, that is, $H_4\,N\,O$), form with the same acids, salts which are isomorphous; the same is the case with potassium and ammonium (Am, that is, $H_4\,N$ or ${}^{v}H_8\,{}^{v}N_2$), with salt-radicals. Thus the sulphates, chromates, nitrates, &c., of potash and oxide of ammonium have the same form, and in many double salts a substitution of the oxide of potassium for oxide of ammonium occurs without any change of form. (See below.) The isomorphism of the potassium and ammonium compounds shows in the clearest manner, that similarity of form does not invariably indicate a like molecular constitution of bodies, for a group of 5 at. of hydrogen, and 1 at. nitrogen (10 at. vol.) has in these compounds the same crystallographic value as a single

atom of potassium. It is very probable, that salts of soda and sodium belong to this group, but that the isomorphism is concealed by dimorphism, except in a few cases. Thus we find soda in soda-alum, in the place of the potash in potash-alum; the crystalline form of both alums is, like their composition, the same, and both crystallize in octahedra. Frankenheim has shown that microscopic crystals of nitrate of potash possess the form of nitrate of soda. It is also conjectured that soda may take the place of potash and lime in the mineral chabasite without any change of form. Anhydrous sulphate of soda, which cannot yet be obtained in the form of sulphate of potash, is exactly isomorphous with sulphate of silver, and the two salts have nearly the same equivalent volume, which differs from the equivalent volume of sulphate of potash and oxide of ammonium. Thus, throughout, the corresponding potassium and ammonium compounds exhibit a great correspondence in their equivalent volume as demanded by isomorphism, but the corresponding sodium compounds are far from being included under the same head, their equivalent volume always approaching nearly to that of the corresponding silver compound. The difference of the equivalent volumes of the analogous but non-isomorphous potassium and sodium compounds is so great—the equivalent volumes standing for the most part nearly in the relation of 4 : 3—that in the case of dimorphism establishing the isomorphism, very considerable changes must take place in the density in order that the equivalent volumes may become equal. (See Kopp.)

The isomorphism of sulphate of silver and sulphate of soda is corroborative of the present atomic weight of silver, whilst, as we have already seen, the isomorphism between Cu_2S and AgS may indicate the propriety of a division of the atom of silver. If, owing to the isomorphism of the latter, we would carry out the division of the silver equivalent into two atoms, in which the oxide of silver would be changed from AgO to Ag_2O, and the dinoxide of silver from Ag_2O to Ag_4O, the division would lead to the halving of the equivalents of the sodium, owing to the isomorphism of the sulphate of soda with sulphate of silver. And these salts would then have the formulæ, Ag_2O, SO_3, and Na_2O, SO_3, and since

there probably exists an isomorphism of sodium compounds with the potassium and ammonium compounds, the equivalents of the potassium and ammonium would necessarily be halved. At the time Berzelius gave the formula $^{v}H_4\,^{v}N$ to ammonium, and oxide of ammonium contained, according to him, 2 at. of ammonium and 1 at. of oxygen, a division of the equivalent of potassium might also have been based upon this. Now, Berzelius has certainly more correctly made the atomic weight of ammonium correspond with the atomic weight of potassium, and consequently 1 at. ammonium is, according to him, = 1 eq. of ammonium, namely, $^{v}H_8\,^{v}N_2$.

It has already been stated that similarity of form is not invariably connected with similarity of composition, but that perfect correspondence in form, that is, actual isomorphism, may also take place between bodies, which exhibit a complete difference with respect to their constitution. Carbon, chloride of sodium, arsenious acid, and alum may all crystallize in octahedra, although they have not even a remote resemblance in composition.

Even if we do not admit that the ordinary occurrence of the simple form of the cube and the regular octahedron, proves the existence of isomorphism, except in cases where we might expect to meet with it, in consequence of well-grounded similarity of composition, as in the different kinds of alum, the isomorphous groups we have been considering, present us with examples of identity of form, without indicating any well-grounded resemblance in the composition, against which the objection in question cannot be urged. Thus the dimorphous bisulphate of potash, $K\,O,\ S\,O_3 + H\,O,\ S\,O_3$, is in one form isomorphous with sulphur of the Fifth System, and in the other form with felspar. Nitrate of soda, $Na\,O,\ N\,O_5$, has the form of calc-spar, $Ca\,O,\ C\,O_2$. The crystals of nitrate of potash, $K\,O,\ N\,O_5$, known under the name of saltpetre, have the form of arragonite, consequently that of the other form of carbonate of lime, and microscopic crystals of this salt, as already observed, occur in the form of nitrate of soda, consequently in that of calc-spar. Finally, anhydrous sulphate of soda, (and oxide of silver, see above,) $Na\,O,\ S\,O_3$, are not isomorphous with manganate of baryta, $Ba\,O,\ Mn\,O_3$, but

with permanganate of baryta, Bn O, $Mn_2 O_7$. In the two first-named bodies the bisulphate of potash and sulphur, the absence of all analogy is obvious. There is not either any resemblance in the composition of nitrate of potash and carbonate of lime, or between permanganate of baryta and sulphate of soda, if we abide by the common views regarding the constitution of these salts.

Attempts have been recently made, from various quarters, to deduce the isomorphism of these salts from the law established by Mitscherlich; but these attempts must for the present be regarded as mere speculations. Thus Schaffgotsch recommends the division of the equivalents of silver, sodium, and potassium into two atoms, and then avails himself of it to explain the isomorphism of the nitrates of potash and soda with carbonate of lime. If, for instance, we exhibit the composition of nitrate of potash, in accordance with the binary theory of the salt, by the formula K, $^{v}N_2 O_6$, it will be after the halving the equivalent of the potassium, K_2, $^{v}N_2 O_6$, or K, $^{v}N O_3$. As, according to this theory, carbonate of lime has the formula Ca, $C O_3$, the analogy of the composition of nitrate of potash and of carbonate of lime is made apparent, $K + {}^{v}N O_3$ and $Ca + C O_3$. The same is the case with nitrate of soda. We perceive by this, that the division of the equivalent of the nitrogen into 2 at., as required by isomorphism, may be supported.

The dimorphism of carbonate of lime and nitrate of potash may possibly, according to Schaffgotsch, be grounded upon the fact, that calc-spar and the nitrate of potash crystallized in this form may be composed according to the formulæ $Ca_2 + C_2 O_6$ and $K_2 + {}^{v}N_2 O_6$, while arragonite and common nitrate of potash have the formulæ $Ca + C O_3$ and $K + {}^{v}N O_3$. Dimorphism would, therefore, be a consequence of polymerism.

In opposition to this Clark proposes doubling the atomic weights of sodium and silver, in order to explain the isomorphism between sulphate of soda, sulphate of silver, and permanganate of baryta. If we carry out this doubling, we have as follows:—

Sulphate of soda....	.... Na + 2S + 8O
Sulphate of silver	.... Ag + 2S + 8O
Permanganate of baryta	.... Ba + 2Mn + 8O

or according to the binary theory of salts,

Sulphate of soda	$Na + 2S O_4$
Sulphate of silver	$Ag + 2S O_4$
Permanganate of baryta	$Ba + 2Mn O_4$

or finally,

Sulphate of soda	$Na O_2 + 2S O_3$
Sulphate of silver	$Ag O_2 + 2S O_3$
Permanganate of baryta	$Ba O_2 + 2Mn O_3$

Isomorphism is, consequently, deduced from a like number, and a like arrangement of the atoms.

We will now after these remarks turn to the consideration of new groups of isomorphous salts. The ordinary green vitriol is a sulphate of the protoxide of iron with 7 equiv. of water, $Fe O, S O_3 + 7 H O$; with the same quantity of water, the sulphate of the protoxide of cobalt crystallizes at an ordinary temperature, while sulphate of protoxide of manganese crystallizes below 6° C. The crystalline form of these three salts is the same, of the Fifth System: they are isomorphous. Sulphate of magnesia and sulphate of zinc likewise crystallize at the ordinary temperature with 7 equiv. of water, (the magnesian salt, $Mg O, S O_3 + 7 H O$, the zinc salt, $Zn O, S O_3 + 7 H O$,) as also sulphate of nickel below 5° C. These three salts are isomorphous with each other, and have an approximatively equal equivalent volume, but they are not isomorphous with the three first-named, as their crystals belong to the Fourth System. The difference of form of these two groups of salts, with similar constitution, may possibly be dependant upon dimorphism; thus it may be, that under certain circumstances the three last salts crystallize in the Fifth System or three first in the Fourth System. It is also understood, that the nickel salt separates from its solution above 30° C. with 7 equiv. of water, in crystals of the Fifth System, whence it would appear, that the salt is trimorphous. But from a solution above 30° C. the manganese and zinc salts crystallize with 6 equiv. of water, in the Fifth System, and of the same form. The sulphate of magnesia crystallizes between 20° and 30°, with 4 equiv. of water, and the sulphate of iron also at 80°, both in the Fourth System, and isomorphous. (Regnault.) Sulphate of copper with 5 equiv. of water, $Cu O, S O_3 + 5 H O$, crystallizes in forms of

the Fifth System; the sulphate of manganese crystallizes with the same quantity of water, and in the same form, under 20°. It is very probable, if not certain, that the sulphates of all the above-named bases, that is, of magnesia, the protoxide of iron, manganese, cobalt, and nickel, zinc, and copper, with the same quantity of water, are isomorphous; but that the isomorphism is in some cases concealed by dimorphism, and in others it has not been made known from want of acquaintance with the circumstances in which the salts of these bases may exist with particular proportions of water. Sulphate of iron crystallizes, as has already been stated, at the usual temperature with 7 equiv. of water, in the Fifth System; and sulphate of copper, with 5 equiv. of water, in the Sixth System. It is probable that, under circumstances with which we are at present unacquainted, the former may separate with the proportion of water and the form of the latter, and the latter may separate with the water and the form of the first. This appears to be proved by a mixed solution of the sulphate of iron and copper yielding a mixed crystal with the water and form of the sulphate of iron. The same holds good with reference to a solution of the sulphate of iron mixed with the sulphates of cobalt and zinc. In the process of smelting copper in the Mansfeld district in Germany, a salt is obtained by washing the copper ore, with 7 equiv. of water, in large violet crystals, of the form of sulphate of iron, in which the bases are oxides of copper, iron, cobalt, manganese, zinc, and magnesia. (See Rammelsberg, *Lehrbuch der Stöchiometrie.*)

It is interesting and worthy of remark, that light blue crystals are yielded by a mixed solution of sulphate of zinc ($Zn\,O,\,S\,O_3+7\,H\,O$,) and sulphate of copper, ($Cu\,O,\,S\,O_3+5\,H\,O$,) which have not the form of either of these salts, but that proper to sulphate of iron, ($Fe\,O,\,S\,O_3+7\,H\,O$,) and which contain like it 7 equiv. of water $\left\{\begin{matrix}Cu\,O\\Zn\,O\end{matrix}\right\}S\,O_3+7\,H\,O$. If a crystal of sulphate of iron is placed in such a mixed solution, it is enlarged by the matter of the double salt, as if by its own, exhibiting a bluish green nucleus, and a light blue external layer; and thus we may obtain it formed of alternating coloured layers by applying alternately a pure solution of the

sulphate of iron and of the mixed solution. Instead of sulphate of zinc we may make use of sulphate of nickel or sulphate of magnesia, with the same results. (Mitscherlich.)

The fact that sulphates of these bases, of like constitution, are isomorphous, is confirmed by the circumstance, that the double salts they form with sulphate of potash and oxide of ammonium, are accurately isomorphous, and have precisely the same composition. All contain 1 equiv. of the alkaline sulphate and 6 equiv. of water; for instance,—

$$\begin{aligned}
&Mg\,O, S\,O_3 + K\,O, S\,O_3 + 6H\,O\\
&Ca\,O, S\,O_3 + K\,O, S\,O_3 + 6H\,O\\
&Zn\,O, S\,O_3 + K\,O, S\,O_3 + 6H\,O\\
&Ni\,O, S\,O_3 + K\,O, S\,O_3 + 6H\,O\\
&Mg\,O, S\,O_3 + K\,O, S\,O_3 + 6H\,O\\
&\qquad\qquad \&c.
\end{aligned}$$

We observe, that the above-named bases include all those which, combining with carbonic acid, yield the interesting isomorphous group of the spars, with the exception of lime. Here the question naturally arises, is sulphate of lime connected by isomorphism with the sulphates of these bases? The question may be answered in the affirmative. In a sulphate of iron of like form with hydrated sulphate of lime (gypsum), we have a like constitution, (that is, $Fe\,O, S\,O_3 + 2\,H\,O$,) with the sparing solubility of sulphate of lime.

As the bases, which form isomorphous salts with carbonic acid, also behave in like manner with reference to sulphuric acid, the conjecture necessarily forces itself upon us, that all the bases in question, will yield analogous and isomorphous salts, with all acids, a conjecture which is generally confirmed by experience. Thus, hydrated chloride of calcium and chloride of magnesium have a similar constitution, and probably a like form; so also, we have hydrated nitrates of magnesia, manganese, cobalt, copper, and zinc, of similar composition; and have reason to suppose, that magnesia, lime, protoxide of iron, protoxide of manganese, frequently replace each other, in the case of the silicates, as for instance in augites.

If we compare the isomorphism of the sulphates which have just been considered, with reference to the equivalent volume of the bases and metals which they contain, we shall arrive at results similar to those that have already been ob-

tained in the salts of baryta, strontia, and lead. The equiv. vols. of Fe, Mn, Co, Ni, Cu, are equal, namely 44; an equiv. of manganese may, therefore, directly replace 1 equiv. of iron, without any change of form occurring, since each fills the same space. So also with Co, Ni, and Cu. The equiv. vol. of zinc is, however, 58, that of cadmium 81, that of magnesium 84, (spec. gravity = 1·87); a substitution of any one of these metals for another, equivalent for equivalent, is, therefore, only possible without any change of form occurring, provided condensation takes place; moreover, the equivalent volumes of the basic oxides, R O of these metals, have not all like equivalent volumes; at least, not so far as the data of which we are now in possession allow of our judging, but it is a remarkable fact, that the equivalent vols. of Mg O and Cu O are almost identical, so that, consequently, although Cu and Mg cannot replace each other, Cu O and Mg O may do so without any change of form occurring. The equiv. vol. of oxide of zinc is larger than that of the last two oxides, but anhydrous sulphate of zinc and sulphate of magnesia, have nearly the same equiv. vol. (Kopp, op. cit., p. 10.)

Graham is of opinion, that the water stands in an isomorphous relation with the bases of these groups, equivalent for equivalent; the isomorphism is certainly not proved, but the resemblance, which in a chemical point of view, water exhibits towards these bases, indicates that such is the case. Thus, according to that chemist, nitrate of copper, hydrated nitric acid of spec. grav. 1·42 and sub-nitrate of copper, are expressed by the formulæ

$$\begin{aligned} &Cu\,O, N\,O_5 + 3H\,O \\ &H\,O, N\,O_5 + 3H\,O \\ &Cu\,O, N\,O_5 + 3(Cu\,O, H\,O) \end{aligned}$$

Crystallized oxalic acid, or oxalate of oxide of hydrogen, corresponds with oxalate of magnesia; hydrated sulphuric acid, $H\,O, S\,O_3 + H\,O$, corresponds with sulphate of magnesia, $Mg\,O, S\,O_3 + H\,O$, and this similarity, in a chemical point of view, is regarded by Graham as a main objection to the division of the equivalent of hydrogen into 2 atoms.

Very recently Scheerer has brought water into an isomorphous relation with the same bases in a totally different

manner; he shows that 3 atoms of H O, have frequently, in a crystallographical and also a chemical relation, the same value as 1 at. Mg O, Fe O, Mn O, and probably also as Ca O, Ni O, Zn O; and that in like manner, 2 at. of H O correspond to 1 atom Cu O. (Poggendorff's *Annalen*, 1846, Bd. 68, s. 319, &c.) The examination of two minerals, cordierite of Krageröe and aspasiolite, led to the discovery of this species of isormorphism, named by Scheerer, polymeric isomorphism. The analysis gave the mean as follows:—

	Cordierite.		Aspasiolite.
Silica	50·44	.....	50·40
Alumina	32·95	.....	32·38
Magnesia	12·76	.....	8·01
Lime	1·12	.....	trace
Protoxide of Iron	0·96	.....	2·34
Protoxide of Manganese	trace	.....	trace
Water	1·02	.....	6·73
	99·25		99·86

If we consider the iron in cordierite as sesquioxide of iron, a view favoured by its deficiency of colour, the relation of the oxygen of the silica ($Si O_3$) to the oxygen of the bases $R_2 O_3$ and R O is as follows:—

$Si O_3$		$R_2 O_3$		R O
26·20	.....	15·64	.....	5·26

which very nearly corresponds to the formula $3R O, 2Si O_3 + 3(R_2 O_3, Si O_3)$; consequently, the relations of oxygen would be 26·20, 15·72, 5·24.

The green colour of aspasiolite indicates the presence of protoxide of iron, which has been confirmed by quantitative analysis. The relation of the oxygen is consequently thus computed:—

$Si O_3$		$R_2 O_3$		R O		H O
26·18	.....	15·12	.....	3·63	.....	5·98

All attempts to deduce a formula from this in the usual manner, fail, and we obtain improbable expressions showing no harmony with the formula of cordierite, to which, however, aspasiolite stands in the closest relation. The two minerals possess the same crystalline forms; rhombic prisms of 120°, with combinations of $O P' \infty \bar{P} \infty$ and $\infty \bar{P} \infty$; the most com-

plete transitions from the one mineral to the other present themselves in the same specimen, and there are crystals partly consisting of aspasiolite and partially of cordierite. The nucleus especially is formed of the latter, and distributes itself, as may be discerned with certainty, by its difference in hardness and colour.

On comparing the composition of aspasiolite with the cordierite of Krageröe, we find that the silica and alumina stand nearly in the same relation in both minerals, and that it is mainly owing to the diminished quantity of magnesia attributable to the large quantity of water, that the mixture of the former differs from that of the latter. It naturally, therefore, occurs to the mind, that both minerals, cordierite and aspasiolite, are isomorphous, and that this isomorphism is owing to a certain quantity of water being able to replace a certain quantity of magnesia. We find by computation, that in such a case, *three* equivalents of water replace *one* equivalent of magnesia. If, in this relation, we were to substitute magnesia* for the water contained in the aspasiolite, we should obtain the following relation of oxygen for this mineral:

SiO_3		R_2O_3		RO
26·18	.....	15·12	.....	5·63

while that found for the cordierite of Krageröe, is 26·10 : 15·64 : 5·26, and these numbers approximate much more if we reckon a part of the iron of the aspasiolite as sesquioxide, for instance, about the half, as

SiO_3		R_2O_3		RO
26·18	.....	15·52	.....	5·37

It consequently follows, that the similarity in the crystalline

* According to the equivalency of 3 at. of HO to 1 equiv. of MgO, and consequently of $3 \times 112{\cdot}55$ (= 3375) to 258·35, there is for every part by weight of water $\frac{258{\cdot}35}{327{\cdot}5} = 0{\cdot}766$ parts by weight of magnesia. For the 6·73 per cent. therefore, of water contained in the aspasiolite, we must take into account $6{\cdot}73 \times 0{\cdot}766 = 5{\cdot}15$ per cent. of magnesia. For the computations of the relations of the oxygen we need, of course, only divide the quantity of oxygen contained in the water by Z, and add the quotient to the oxygen of the magnesia from which we find, in the case before us, that the whole amount of the oxygen in $RO = 3{\cdot}63 + \frac{1}{3} \times 5{\cdot}98 = 563$.—(Scheerer.)

form of cordierite and aspasiolite may be explained by the assumption, that 3 equiv. (atoms) of water may isomorphously replace 1 equiv. (1 at.) of magnesia. The manner in which this substitution is effected has been shown by Scheerer in the interesting work alluded to, by reference to a large series of minerals and compounds. If we reckon from the analysis of the different forms of serpentines, the quantity of oxygen in the bases, R O, and that of the water, H O, and add to them in the manner indicated, (that is, by taking from the amount of the oxygen of the water $\frac{1}{3}$ 3H O = R O) the sum will in all cases be equal to the oxygen contained in the silica, and hence we have for all forms of serpentine the simple formula of (R O), $3Si O_3$. The insertion of the R O means, that in this portion, a larger or smaller part of the magnesia, and its isomorphous base (Ḟe, Ṁn, &c.,) is replaced by water in the relation indicated. This formula is, however, that for olivine (3R O, $Si O_3$) with this difference only, that in the latter no magnesia is replaced by water. Serpentine may therefore be regarded as hydrated olivine, and hence we have an explanation of the reason that crystallized serpentine (of Snarum) has the same crystalline form as olivine.

The doubly refracting datolite, for which Rammelsberg has given the formula 2 ($3Ca O, Si O_3, +3B O_3, Si O_3 + 3 H O,$) in which boracic acid plays the part of a base, has, according to Scheerer's view, the formula $3(\dot{C}a\ \ddot{S}i + \dot{C}a\ \ddot{B}) + (\dot{R})\ \ddot{S}i$. The combinations of magnesia with carbonic acid and water (magnesia alba, &c.) come to have in the same way very simple formulæ. In the magnesian sulphates, containing 7 equiv. of water, 1 equiv. always occurs as water of crystallization, while 6 equiv. (=2Ṙ,) are combined as bases with the sulphuric acid. Graham observed that these 6 equiv. of water escape with considerably more facility than the seventh equivalent. He called the latter *constitutional* water, and the former water of crystallization; but, according to Scheerer's mode of observation, we must invert these terms. As I shall have occasion to revert to Scheerer's admirable treatise, I must be permitted to remark, that it would not have lost in any way, if the author had refrained from extending polymeric isomorphism (although only provisionally,) to magnesian sulphates and similar compounds.

The isomorphous group of the alums, which has already been mentioned at page 122, ranges itself with both the preceding isomorphous groups. The general formula for alums is R O, $S O_3 + R_2 O_3$, $3S O_3 + 24H O$, or shorter $\dot{R}\,\ddot{S}$, $\dot{R}\,\dot{R}\,\ddot{S}_3 + 24\,\dot{H}$; $R_2 O_3$ may be alumina, sesquioxide of iron, sesquioxide of chromium, sesquioxide of manganese, (common alum, iron alum, chrome alum, manganese alum); and R O may be potash, oxide of ammonium, or soda, (potash alum, ammonia alum, soda alum). Common alum is, for the most part, potash-and-alumina alum, and the formula is consequently as follows:—

$\dot{K}\,\ddot{S} + \dot{Al}\,\dot{Al}\,\ddot{S}_3 + 24H O.$

Ammonia and iron alum is $\dot{Am}\,\ddot{S} + \dot{Fe}\,\dot{Fe}\,\ddot{S}_3 + 24H O.$

Potash and chrome alum is $\dot{K}\,\ddot{S} + \dot{Cr}\,\dot{Cr}\,\ddot{S}_3 + 24H O.$

All these alums occur in octahedra, and their equivalent volumes are all equal. In this case we also see that isomorphism of the constituents is not the necessary result of isomorphism of the combinations. The sesquioxides of iron and chromium and alumina have the same equivalent volume, and may, therefore, directly replace each other, equivalent for equivalent, without the forms being deranged, but the metals, chromium and aluminum, have a different equivalent volume from iron.

Reciprocal substitution of these atoms amongst themselves, without any change of form, occurs as frequently in the sesquioxides as among the protoxides belonging to the magnesian group; and it is most clearly indicated in those spinell-like minerals that crystallize in the regular system, in which the sesquioxides are contained as negative constituents. The type of this group of minerals is as follows:—

Spinell	$\dot{Mg}\,\dot{Al}\,\dot{Al}$
Pleonast	$\overset{\frown}{\dot{Mg}\,\dot{Fe}}\,\dot{Al}\,\dot{Al}$
Gahnite	$\overset{\frown}{\dot{Zn}\,\dot{Mn}\,\dot{Fe}}\,\dot{Al}\,\dot{Al}$
Magneticum	$\dot{Fe}\,\dot{Fe}\,\dot{Fe}$
Chrome iron-stone	$\overset{\frown}{\dot{Fe}\,\dot{Mg}}\,\overset{\frown}{\dot{Cr}\,\dot{Al}}$
Franklinite	$\overset{\frown}{\dot{Mn}\,\dot{Fe}\,\dot{Zn}}\,\overset{\frown}{\dot{Fe}\,\dot{Mn}}$

As the concluding isomorphous group, we may mention the one which is composed of the double chlorides, from the union of chloride of potassium, or chloride of ammonium, with the chlorides of platinum, palladium, iridium, and osmium; to which belong chloride of potassium and platinum, K Cl, Pt Cl_2; chloride of ammonium and platinum, Am Cl, Pt Cl_2; chloride of potassium and palladium, K Cl, Pd Cl_2, &c. These double chlorides crystallize together in octahedra, and have a similar constitution. As the equivalent volumes of these four metals are equal, we may derive the isomorphism of the double chlorides from the isomorphism of the metals.

Chemists have always been very desirous of finding some simple physical characteristic, by which to ascertain the atomic weights; and identity of volume in a gaseous condition, identity of specific heat, and similarity in the crystalline form, have in turn been esteemed as certain means of recognition.

At the proper places we have already spoken at large upon the subject of the two first-named characteristics, and stated that, although they must not be left wholly out of the question, they nevertheless cannot serve as generally available aids in determining the atomic weight.

The question as to whether isomorphism may serve, unconditionally, as a means of determining the atomic weight, and whether, consequently, the differences of the atomic weights which it enforces, must, in all cases, be directly taken into account, will be answered by the consideration of the isomorphous groups. It cannot be denied, that the indications of isomorphism agree better than those of specific heat, and better than the weight of the volumes with those views of the constitution of bodies, which have been derived from purely chemical considerations; and they are most invaluable in establishing an analogy of composition in a group of bodies; whilst they afford us an exact characteristic, that may be explained by numbers, in the place of the common and ill-determined resemblance between compounds, which has been observed by chemists more from a practised tact than from rule, and which has hitherto been their only guide in classification. If, therefore, we admit that isomorphism is a certain test of the resemblance of atomic constitution, within the limits of a group

of elements and their compounds, we must, nevertheless, question whether the relation of the atoms to the crystalline form is, without exception, the same throughout the whole series of the elements, or whether all agree exactly in this or any other physical property.

It is even possible that the crystalline form and isomorphism may not be the consequence of the atomic constitution, or that they are not immediately and necessarily connected with it, but, on the contrary, they may arise from a secondary property of bodies, in which a single atom may accidentally resemble a compound body. This seems to be proved by sulphur in one of its two forms being isomorphous with bisulphate of potash, and that a single atom of potassium is isomorphous throughout a long series of combinations with the group of 5 atoms composing ammonium. The last circumstance, as well as the isomorphism of the cyanogen compounds with the chlorine compounds, (Hg Cy and Hg Cl,) shows, at any rate, clearly, that the compound radicals have the same value in an isomorphous relation as the simple radicals,—the elements. It must also be remarked, that Will has exhibited a quinine-and-iron alum; and that, according to Ortigosa, there probably exists an alum, which, in the place of R O, contains the alkaloid conine, (C_{16} H_{16} N.)

The dimorphism of simple as well as compound bodies also indicates the subordinate character of the crystalline form. Is it probable that sulphur and carbonate of lime could by merely a trifling difference of temperature be brought to yield totally different crystals, if form were the result of an unchangeable atomic constitution? The crystalline form is perhaps dependent upon a property of bodies, with which we are as yet unacquainted, and which may stand in a frequent and general, although not invariable, relation to their atomic condition. If this be granted, it will not be at variance with the doctrine of isomorphism, if one atom of a certain group of elements possess the same crystallographic value as two or more atoms of another group. (Graham.)

Truly isomorphous bodies resemble each other in many other properties besides form. The corresponding arseniates and phosphates agree in taste, in the degree of force with

which they retain water of crystallization and in various other properties. Seleniate and sulphate of soda, isomorphous compounds, are both efflorescent salts, and their resemblance, with regard to their solubility in water, goes so far, that both show the unusual deviation from the law of increase of solubility at higher temperatures, of being more easily soluble in water at 92° F., than in water heated to the boiling-point. It certainly appears that isomorphism is always accompanied by a resemblance in many other properties, and it seems as if it were a feature indicative of the closest relationship between two bodies.

It will subsequently be shown that bodies act more readily upon each other as solvents, and admit of being mixed in a fluid form, in proportion to the similarity existing in their composition. Attraction towards another possessing a similar character with themselves, is probably the reason that the particles of isomorphous bodies blend so readily together, and on this may depend the difficulty of separating them, when they are once dissolved in a common solvent. Permanganate and perchlorate of potash, isomorphous salts, may certainly crystallize apart from the same solution, owing to their solubility being so different; and potash alum may, by crystallization, be freed from the greatest part of the iron alum contained in it, because the latter is more easily dissolved, and remains in the mother-liquid; but most isomorphous salts, for instance, sulphate of protoxide of iron and sulphate of copper crystallize when they are dissolved together, yielding not distinct, but homogeneous, crystals, which are a mixture of both salts in indefinite proportions. This blending of isomorphous salts is very frequently found in minerals, as we have already seen; it was wholly inexplicable, and seemed to be entirely at variance with the theory of equivalents until the capacity of isomorphous bodies to crystallize in common was recognised as a natural law. If isomorphism have only a limited value in the determination of the atomic numbers of bodies, it follows, as has already been stated, that the chemist is especially led to adhere to the equivalents. I again repeat, the more the investigator divides the equivalents in order to bring them in accordance with the physical properties of

bodies, the more will these atoms yield in chemistry to chemical atoms, that is, to the equivalent atoms.

The relative equivalents of bodies resembling each other chemically admit, generally speaking, of being ascertained with the greatest certainty; not so, however, with respect to the relative equivalents of elements of heterogeneous chemical character. There can be no doubt as to the relative quantities required in the reciprocal substitution of chlorine, iodine, bromine, oxygen, sulphur; nor as to the same quantities in hydrogen, potassium, magnesium, calcium, barium, iron, &c.; nor the quantities by weight of antimony and arsenic, or even perhaps of phosphorus and nitrogen, which may replace each other. But what, for instance, is the quantity of nitrogen or phosphorus, or arsenic, necessary to take the place of 100 parts of oxygen? This is another question. Have the elements a different equivalent in different combinations? are they influenced by allotropism?

Graham, who always deduces isomorphism of combinations from isomorphism of the constituents, which naturally leads us at last to the isomorphous elements, has divided these elements into isomorphous groups. As in the formation of these groups, the isomorphism of the combinations must necessarily serve as a guiding point throughout these combinations, they must be of interest even to those chemists, who do not admit without some reservation that isomorphism of the combinations results from isomorphism of the constituents, embracing as they do such elements as are connected together by the isomorphism of their compounds. This mode of grouping cannot therefore be passed by without some short notice.

Classification of Elements, (Graham).

The extent to which the isomorphous relations of bodies have been traced, will appear on reviewing the groups or natural families in which the elements may be arranged, and observing the links by which the different groups themselves are connected; these classes not being abruptly separated, but shading into each other in their characters, like the classes created by the naturalist for the objects of the organic world.

I. *Sulphur Class.*—This class comprises four elementary bodies: oxygen, sulphur, selenium, tellurium. The three last of these elements exhibit the closest parallelism in their own properties, in the range of their affinities for other bodies, and in the properties of their analogous compounds. They all form gases with one atom of hydrogen, and powerful acids with three atoms of oxygen, of which the salts, the sulphates, seleniates, and tellurates are isomorphous; and the same relation undoubtedly holds in all the corresponding compounds of these elements.

Oxygen has not yet been connected with this group by a certain isomorphism of any of its compounds; but a close correspondence between it and sulphur appears, in their compounds with one class of metals being alkaline bases of similar properties, forming the two great classes of oxygen and sulphur bases, such as oxide of potassium and sulphide of potassium; and in their compounds with another class of elements being similar acids, giving rise to the great classes of oxygen and sulphur acids, such as arsenious and sulpharsenious acids. They farther agree in the analogy of their compounds with hydrogen, particularly of binoxide of hydrogen and bisulphide of hydrogen, both of which bleach, and are remarkable for their instability; and in the analogy of the oxide, sulphide, and telluride of ethyl, and of alcohol and mercaptan, which last is an alcohol with its oxygen replaced by sulphur. This class is connected with the next by manganese, of which manganic acid is isormorphous with sulphuric acid, and consequently manganese with sulphur.

II. *Magnesian Class.*—This class comprises magnesium, calcium, manganese, iron, cobalt, nickel, zinc, cadmium, copper, hydrogen, chromium, aluminum, glucinum, vanadium, zirconium, yttrium, thorinum. The protoxides of this class, including water, form analogous salts with acids. A hydrated acid, such as crystallized oxalic acid or the oxalate of water, corresponding with the oxalate of magnesia in the number of atoms of water with which it crystallizes, and the force with which the same number of atoms is retained at high temperatures; hydrated sulphuric acid ($HO, SO_3 + HO$) with the sulphate of magnesia ($MgO, SO_3 + HO$). The isomorphism of the

salts of magnesia, zinc, cadmium, and the protoxides of manganese, iron, nickel, and cobalt, is perfect. Water (H O) and oxide of zinc (Zn O) have both been observed in thin regular six-sided prisms; but the isomorphism of these crystals has not yet been established by the measurement of the angles. Oxide of hydrogen has not, therefore, been shown to be isomorphous with these oxides, although it greatly resembles oxide of copper in its chemical relations. Lime is not so closely related as the other protoxides of this group, being allied to the following class. But its carbonate, both anhydrous and hydrated, its nitrate, and the chloride of calcium, assimilate with the corresponding compounds of the group; while to its sulphate or gypsum, Ca O, $S O_3$ + 2H O, one parallel and isomorphous compound, at least, can be adduced, a sulphate of iron, Fe O, $S O_3$ + 2H O (Mitscherlich), which is also sparingly soluble in water, like gypsum. Glucina is isomorphous with lime from the isomorphism of the minerals euclase and zoisite. (Brooke.)

The salts of the sesquioxide of chromium, of alumina, and glucina, are isomorphous with those of sesquioxide of iron ($Fe_2 O_3$), with which these oxides correspond in composition; and the salts of manganic and chromic acids are isomorphous, and agree with the sulphates. The vanadiates are believed to be isomorphous with the chromates. Zirconium is placed in this class, because its fluoride is isomorphous with that of aluminum and that of iron, and its oxide appears to have the same constitution as alumina; and yttrium and thorium, solely because their oxides, supposed to be protoxides, are classed among the earths.

III. *Barium Class.*—Barium, strontium, lead. The salts of their protoxides, baryta, strontia, and oxide of lead, are strictly isomorphous, and one of them at least, oxide of lead, is dimorphous, and assumes the form of lime, and the preceding class in the mineral plumbocalcite, a carbonate of lead and lime. (Johnston.) But certain carbonates of the second class are dimorphous, and enter into the present class, as the carbonate of lime in arragonite, carbonate of iron in junckerite, and carbonate of magnesia procured by evaporating its solution in carbonic acid water to dryness by the water-bath (G. Rose),

which have all the common form of carbonate of strontia. Indeed, these two classes are very closely related.

IV. *Potassium Class.*—The fourth class consists of potassium, ammonium, sodium, silver. The term ammonium is applied to a hypothetical compound of one atom of nitrogen and four of hydrogen ($N H_4$), which is certainly, therefore, not an elementary body, and probably not even a metal, but which is conveniently assimilated in name to potassium, as these two bodies occupy the same place in the two great classes of potash and ammonia salts, between which there is the most complete isomorphism. Potassium and ammonium themselves are, therefore, isomorphous. The sulphates of soda and silver are similiform, and hence also the metals sodium and silver; but their isomorphism with the preceding pair is not so clearly established. Soda replaces potash in soda alum, but the form of the crystal is the common regular octohedron; nitrate of potash has also been observed in microscopic crystals, having the rhomboidal form of nitrate of soda*, which is better evidence of isomorphism, although not beyond cavil, as the crystals were not measured. There are also grounds for believing that potash replaces soda in equivalent quantities in the mineral chabasite, without change of form. The probable conclusion is, that potash and soda are isomorphous, but that this relation is concealed by dimorphism, except in a very few of their salts.

This class is connected in an interesting way with the other classes through the second. The subsulphide of copper and the sulphide of silver appear to be isomorphous, although two atoms of copper are combined in the one sulphide, and one atom of silver in the other, with one atom of sulphur; their formulæ being—

$$Cu_2 S \text{ and } Ag S.$$

Are then *two* atoms of copper isomorphous with *one* atom of silver? In the present state of our knowledge of isomorphism, it appears necessary to admit that they are.

* Frankenheim, in Poggendorf's *Annalen*, vol. xl., page 447. See also a paper by Professor Johnston on the received equivalents of potash, soda, and silver; Phil. Mag., third series, vol. xii., p. 324.

The fourth class will thus stand apart from the second, which is represented by copper, and also from the other classes connected with the second, in so far as one atom of the present class is equivalent to two atoms of the other classes in the production of the same crystalline form. This discrepancy may be at once removed by halving the atomic weight of silver, and thus making both sulphides to contain two atoms of metal to one of sulphur. But the division of the equivalents of sodium, potassium, and ammonium, which would follow that of silver, and the consideration of potash and soda as suboxides, are assumptions not to be lightly entertained.

It was inferred by M. Mosander, that lime with an atom of water is isomorphous with potash and soda, because Ca O + H O appears to replace K O or Na O in mesotype, chabasite, and other minerals of the zeolite family. The isomorphism of natrolite and scolezite is so explained: Na O, $Al_2 O_3$, $2Si O_3$, 2H O with Ca O, $Al_2 O_3$, $2Si O_3$, 3H O. On the other hand, it is strongly argued by M. T. Scheerer, that one equivalent of magnesia is isomorphous with three equivalents of water, from the equality of the forms of cordierite and a new mineral aspasiolite, the first containing Mg O, and the second 3H O in its place; and from a review of a considerable number of alumino-magnesian minerals. One equivalent of oxide of copper, however, is supposed to be replaced by two equivalents of water.

V. *Chlorine Class.*—Chlorine, iodine, bromine, fluorine. These four elements form a well-defined natural family. The three first are isomorphous throughout their whole combinations —chlorides with bromides and iodides, chlorates with bromates and iodates, perchlorates with periodates, &c.; and such fluorides also as can be compared with chlorides appear to affect the same forms. The fluoride of calcium of apatite, Ca F, $3(3Ca O, P O_5)$, is also replaced by the chloride of calcium. It is connected with the second class through perchloric acid; the perchlorates being strictly isomorphous with the permanganates. But the formulæ of these two acids are—

$$Cl O_7 \text{ and } Mn_2 O_7,$$

one atom of chlorine replacing two atoms of manganese. Or,

this class has the same isomorphous relation as the preceding class to the others: and such I shall assume to be its true relation. Although halving the atomic weight of chlorine, which would give two atoms of chlorine to perchloric acid, is not an improbable supposition, still it would lead to the same strange conclusion as follows the division of the equivalent of sodium,—namely, that chlorine enters into its other compounds, as well as into permanganic acid, always in the proportion of two atoms; for that element is never known to combine in a less proportion than is expressed by its presently received equivalent. Cyanogen ($C_2 N$), although a compound body, has some claim to enter this class, as the cyanides have the same form as the chlorides.

VI. *Phosphorus Class.*—Nitrogen, phosphorus, arsenic, antimony, and bismuth; also composing a well-marked natural group, of which nitrogen and bismuth are the two extremes, and of which the analogous compounds exhibit isomorphism. These five elements all form gaseous compounds with three atoms of hydrogen; namely, ammonia, phosphuretted hydrogen, arsenietted hydrogen, &c. The hydriodates of ammonia and of phosphuretted hydrogen are not, however, isomorphous. Arsenious acid and the oxide of antimony, both of which contain three atoms of oxygen to one of metal, are doubly isomorphous. Arsenious acid also is capable of replacing oxide of antimony in tartrate of antimony and potash or tartar emetic, without change of form; and arsenic often substitutes antimony in its native sulphide. The native sulphide of bismuth ($Bi S_3$) is also isomorphous with the sulphide of antimony ($Sb S_3$). Nitrous acid ($N O_3$), which should correspond with arsenious acid and oxide of antimony, likewise acts occasionally as a base, as in the crystalline compound with sulphuric acid of the leaden chambers. The complete isomorphism of the arseniates and phosphates has already been noticed. But phosphoric acid forms two other classes of salts, the pyrophosphates and metaphosphates, to which arsenic acid supplies no parallels.

This class of elements is connected with the others by means of the following links:—Bisulphide of iron is usually cubic, or of the regular system; but it is dimorphous, and, in

sperkise, it passes into another system, and has the form of arsenide of iron; $Fe S_2$, or rather $Fe_2 S_4$, being isomorphous with $Fe_2 As S_2$. Again, bisulphide of iron, in the pentagonal-dodecahedron of the regular system, is isomorphous with cobalt-glance, $Fe_2 S_4$ with $Co_2 As S_2$: so that one equivalent of arsenic appears to be isomorphous with 2S. This is also supported by the isomorphism of the sulphide of cadmium and sulphide of nickel (Cd S and Ni S, or $Cd_2 S_2$ and $Ni_2 S_2$), with the arsenide of nickel ($Ni_2 As$). Tellurium has also been observed in the same form as metallic arsenic and antimony. The phosphorus class approximates also to the chlorine class; nitrogen and chlorine both forming a powerful acid with five equivalents of oxygen, nitric acid, and chloric acid; but of the many nitrates and chlorates which can be compared, no two have proved isomorphous. Nor do the metaphosphates appear at all like the nitrates, although their formulæ correspond.

Nitrogen, it must be admitted, is but loosely attached to this class. It is greatly more negative than the other members of the class, approaching oxygen in that character, with which, indeed, nitrogen might be grouped, N being equivalent to 2O. For while phosphuretted hydrogen is the hydride of phosphorus, or has hydrogen for its negative and phosphorus for its positive constituent, ammonia is undoubtedly the nitride of hydrogen, or has nitrogen for its negative and hydrogen for its positive constituent. The one should be written PH_3, and the other $H_3 N$—a difference in constitution which separates these bodies very widely. An important consequence of classing nitrogen with oxygen is, that, in the respective series of compounds of these elements, cyanogen becomes the analogue of carbonic oxide, $C_2 N$ being equivalent to C O, or, rather $C_2 O_2$.

VII. *Tin Class.*—Tin, titanium. Connected by the isomorphism of titanic acid ($Ti O_2$) in rutile with peroxide of tin ($Sn O_2$) in tin-stone. Titanium is connected with iron and the second class. Ilmenite and other varieties of titanic iron which have the crystalline form of the sesquioxide of that metal,—namely, that of specular iron, and also of corundum (alumina),—are mixtures of a sesquioxide of titanium ($Ti_2 O_3$) with sesquioxide of iron (H. Rose).

VIII. *Gold Class.*—Gold, which is isomorphous with silver in the metallic state. Gold will thus be connected, through silver, with sodium and the fourth class.

IX. *Platinum Class.*—Platinum, iridium, osmium. From the isomorphism of their double chlorides. The double bichloride of tin and chloride of potassium crystallizes in regular octahedrons, like the double bichloride of platinum and potassium, and other double chlorides of this group; which, although not alone sufficient to establish an isomorphous relation between this class and the seventh, yet favours its existence (Dr. Clark). The alloy of osmium and iridium (Ir Os) is isomorphous with the sulphide of cadmium (Cd S) and sulphide of nickel (Ni S) (Breithaupt).

X. *Tungsten Class.*—Tungsten, molybdenum, tantalum, niobium, and pelopium. From the isomorphism of the tungstates and molybdates, the salts of tungstic and molybdic acids, WO_3 and MoO_3. Tantalic acid is isomorphous with tungstic acid: tantalite (FeO, TaO_3) with wolfram (FeO, WO_3). So are molybdic and chromic acids; the tungstate of lime, tungstate of lead, molybdate of lead, and chromate of lead (in the least usual of its two forms), being all of the same form. This establishes a relation between molybdic, chromic, sulphuric, and other analogous acids*. Niobium and pelopium are introduced into this class as they replace tantalum in the tantalites of Bavaria.

XI. *Carbon Class.*—Carbon, boron, silicium. These elements are placed together, from a general resemblance which they exhibit without any precise relation. They are not known to be isomorphous among themselves, or with any other element. They are non-metallic, and form weak acids with oxygen,—the carbonic, consisting of two of oxygen and one of carbon, and the boric and silicic acids, which are generally viewed as composed of three of oxygen to one of boron and silicium. Silicic acid may, perhaps, replace alumina in some minerals, but this is uncertain.

Of the elements which have not been classed, no isomorphous relations are known. They are mercury, which in some

* Johnston, Phil. Mag. 3d series, vol. xii. p. 387.

of its chemical properties is analogous to silver, and in others to copper, cerium, didymium, lanthanum, lithium, rhodium, ruthenium, palladium, and uranium. Ruthenium, however, is believed to be isomorphous with rhodium, from the correspondence in composition of their double chlorides. Didymium and lanthanum are also probably isomorphous with cerium, as they appear to replace that metal in cerite.

V.

PHYSICAL INVESTIGATIONS ON DYEING.

By M. Chevreul.

ON THE INFLUENCE THAT TWO COLOURS MAY EXERCISE UPON EACH OTHER WHEN SEEN SIMULTANEOUSLY.

Introduction.

The investigations I have pursued on the subject of dyeing, considered in the most general and comprehensive point of view, may be classed in three different series.

The first Series embraces, under the head of *physical* enquiries:

1. All that has relation to the principle of the simultaneous contrast of colours: this principle is so infinitely varied, that in spite of my wish to concentrate my labours within the department of chemistry, as applicable to dyeing properly so called, I have been unable to refrain from directing my attention to the establishment of a theory that might serve as a guide in those arts and manufactures, whose object it is to challenge attention by the assortment and arrangement of colours. This will explain how my first article on this subject, published in 1828, and printed in the 11th volume of the *Mémoires de l'Academie*, led me into a course of investigations of such extent that they occupy, together with my previous observations, an octavo volume of 721 pages, which appeared in 1839.

2. A theory of the optical effects of articles of silk.

3. The exposition of a mode of defining and naming colours according to a rational and experimental method.

The Second Series comprises investigations which I term *physico-chemical*, from their depending on the principle of the mixture of colours, which come within the department of physics, and being at the same time connected with chemical actions in all those cases, in which the principle has to be applied to the fixation of several coloured substances on stuffs of different kinds, by means of the process of dyeing.

The Third Series includes my *chemical investigations*, properly so called, on dyeing. Six memoirs have already appeared in the *Recueil des Mémoires de l'Academie*, and are as follows.

First Memoir. An introduction and general considerations on dyeing. Vol. XV., p. 383, *Mémoires de l'Academie.*

Second Memoir. On the proportion of water that various stuffs absorb in atmospheres of 65, 75, 80, and 100 of Saussure's hygrometer. Vol. XV., p. 409. Introduction to the third, fourth, fifth, and sixth Memoirs, Vol. XVI., p. 41.

Third Memoir. On the action of pure water on stuffs dyed with various colouring matters. Vol. XVI., p. 47.

Fourth Memoir. The changes effected by light, atmospheric agents, and hydrogen gas on curcuma or turmeric, sumach, carthamus, archil, saxon blue (sulfo-indigotic acid), indigo, and prussian blue, when impressed on cotton, silk, and woollen stuffs. Vol. XVI., p. 53.

Fifth Memoir. On the changes effected by heat and atmospheric influences on curcuma or turmeric, sumach, carthamus, archil, saxon blue (or sulfo-indigotic acid), indigo, and prussian blue, and other colouring matters impressed on cotton, silk, and woollen stuffs. Vol. XVI., p. 181.

Sixth Memoir. On the several changes of colour experienced by prussian blue when impressed upon different stuffs. Vol. XIX., p. 491.

An appendix to this Memoir, containing some general considerations and inductions relative to the nature of living organized beings.

Seventh Memoir. On the composition of wool; on the theory of clearing wool of the yolk, and some properties de-

rived from its composition, that may influence the arts and manufactures to which it is applied. Read before the Academy, April 20, 1840.

Eighth Memoir. Considerations on the theory of dyeing, and applications of this theory to the perfection of several practical processes in general, and to that of dyeing with indigo in the *blue vat*, in particular. Read before the Academy, November 23, 1846.

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1. The frequent opportunities I have had of observing the very various and strongly contrasting colours, that are required in the royal manufactories of tapestry have enabled me to make some observations, which I trust will not be wholly useless to those whose object it is, by means of an assortment of differently coloured objects, to produce the best possible effect to please the eye. The phenomena of which I shall treat in this paper fall under the head of what natural philosophers term accidental colours, in accordance with the term applied to them by Buffon, who was the first to treat of the subject with any degree of detail; before, however, I enter more fully into the question, I would direct attention to some of the principles of optics that have the most intimate connection with the subject of which I am treating.

2. A ray of solar light is composed of an indeterminate number of differently coloured rays; since, on the one hand, it is impossible to distinguish each in particular, and as, on the other, they do not all differ equally from one another, they have been divided into groups, to which have been applied the terms *red rays, orange rays, yellow rays, green rays, blue rays, indigo rays, and violet rays.* It must not, however, be supposed that all the rays comprised in the same group, as, for instance, in that of the red rays, are identical in colour. On the contrary, they are generally considered as capable of differing more or less among themselves, although we recognise the sensation separately produced by each one as comprised in that which we ascribe to red.

3. When light is reflected by an opaque white body, it does not experience any modification in the proportion of the

different coloured rays, which constitute white light. If this body be not polished, each point of its surface must be considered as radiating in every direction the light falling upon it; and if the body be polished, a regular or specular reflection will be produced, but in this case, as in the former, there will be a certain quantity of light reflected irregularly, or in every direction.

4. When the light is reflected by an opaque coloured body there is always: (1) a reflection of white light, (2) a reflection of coloured light, which is owing to the fact that the body absorbs or extinguishes in its interior a certain number of coloured rays, and reflects others. It is evident that the rays reflected are of a different colour from those that have been absorbed, and besides, that if they were combined with the former, white light would be reproduced. It is this mutual relation possessed by coloured rays of again forming white light by their blending together that has led us to term certain of them as *complementary* of others. Further, it is evident that opaque coloured bodies reflect white and coloured light, both regularly and irregularly, or only irregularly, according as to whether or not they are polished.

5. It would be erroneous to suppose that a red or a yellow body reflected, besides white light, only red or yellow rays; each of these bodies reflects, besides, all kinds of coloured rays; but those rays, which make us believe it to be red or yellow, being more numerous than the others, produce a greater effect; these other rays exercise, however, an incontestible influence in modifying the action of the red or yellow rays upon our organs of vision, and this will explain the innumerable differences of shade which we remark among different red and different yellow bodies, &c.

6. I shall explain in my first paragraph:

1. The manner of observing the phenomena treated of in this memoir:

2. The law of these phenomena, and the formula representing them:

3. The application of the law to a certain number of these phenomena:

4. The effect of colours upon white, and reciprocally of white upon colours:

5. The effect of colours upon black, and reciprocally of black upon colours:

6. The influence of the chemical nature of coloured bodies upon the phenomena observed:

7. The reciprocal influence of different kinds of colours belonging to the same group:

8. The interpretation of the phenomena on the hypothesis that the red, yellow, and blue are simple colours, and that the orange, green, indigo, and violet are compound colours:

9. The connection between my observations on accidental colours and those made by earlier observers:

10. The physiological cause to which the explanation of accidental colours is referred.

I shall treat in a second paragraph of some applications of the preceding observations.

I.

ARTICLE I.—*Manner of observing the Phenomena treated of in this Memoir.*

7. If we look simultaneously at two narrow zones of different colour placed side by side, the colours will be more or less modified. The following is a very simple manner of convincing ourselves of this proposition.

Fig. 1.

8. We take two bands, O and O′, (fig. 1) of the same colour and identical, and two other bands, P and P′, of another colour and identical. They must be 0·5 inch in width, and 2·5 inches in length. They may be formed of some stuff, or of paper, or of ribbon, of the width I have

indicated. We then paste the band O′ with gum to a card, put O at the distance of $\frac{1}{20}$th of an inch and the band P in such a manner that it shall touch O; and finally paste on P′, at the distance of $\frac{1}{20}$th of an inch from P.

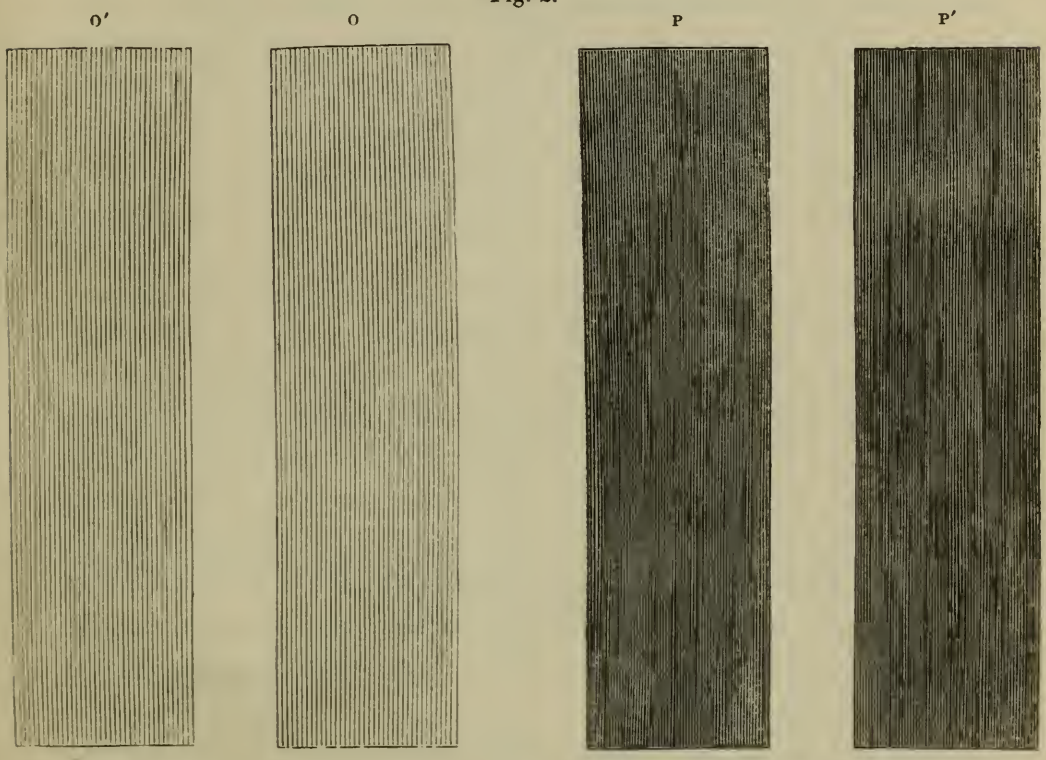
9. Now if we look at the card in a certain direction and during some seconds, we shall almost always see four differently coloured bands. It must be observed that O′ and P′ serve as terms of comparisons to judge of the modifications experienced by O and P in their juxta-position.

10. I give seventeen observations by way of illustration:

Colours used in the Experiment.		Modification.
Red	....	inclining to violet.
Orange	....	„ yellow.
Red	....	„ violet, or less yellow.
Yellow	....	„ green, or less red.
Red	....	„ yellow.
Blue	....	„ green.
Red	....	„ yellow.
Indigo	....	„ blue.
Red	....	„ yellow.
Violet	....	„ indigo.
Orange	....	„ red.
Yellow	....	„ bright green, or less red.
Orange	....	„ red.
Green....	....	„ blue.
Orange	....	„ yellow, or less brown.
Indigo	....	„ blue, or brighter indigo.
Orange	....	„ yellow, or less brown.
Violet	....	„ indigo.
Yellow	....	„ brilliant orange.
Green....	....	„ blue.
Yellow	....	„ orange.
Blue	....	„ indigo.
Green....	....	„ yellow.
Blue	....	„ indigo.
Green....	....	„ yellow.
Indigo	....	„ violet.
Green....	....	„ yellow.
Violet	....	„ red.
Blue	....	„ green.
Indigo	....	„ deep violet.
Blue	....	„ green.
Violet	....	„ red.
Indigo	....	„ blue.
Violet	....	„ red.

11. Before I proceed further, I would wish to draw attention to one of the most important observations recorded in this memoir; namely, that *the reciprocal modifications of colours are not limited to the case where the modifying coloured zones are contiguous to one another, for they may be observed even when the zones are separated.* The following experiment will show this conclusively: take two stripes of the same blue paper, O, O′, (fig. 2) and two stripes of the same green paper, P, P′. The

Fig. 2.



blue and green must be of the same height of tone. The stripes are to be 4 inches in length, and 0·8 inch in width. Place them parallel to one another, in such a manner that O is at 0·44 inch from P, O′ at 0·28 inch from O, and finally P′ at 0·28 inch from P. Standing then at six paces from the card, you will see the colours modified: O will be of a less green blue than O′, and P will be of a green more yellow than P′.

I shall frequently have occasion to revert to this remarkable fact.

ARTICLE II.—*Law of the preceding Phenomena, and the Formula representing them.*

12. After having satisfied myself that the above-mentioned phenomena were constantly presented to my sight when not fatigued, and that many persons accustomed to judge of colours saw them as I did, I endeavoured to reduce them to some sufficiently general expression to enable one to foresee the effect that would be produced upon the organ of sight by the juxtaposition of two given colours. All the phenomena that I have observed seem to me to depend upon a very simple law, which, taken in its most general signification, may be expressed in these terms: *in the case of the eye seeing at the same time two colours which are in contact, they will appear as dissimilar as possible.*

13. From what I have said of the complementary colours, it is evident that the colour of the stripe O (fig. 1) will differ as much as possible from that of the stripe P, when the complementary colour of P is added to the colour of O; in like manner, the colour of P will differ in the greatest possible degree from the colour of O, when the complementary colour of the latter is added to the colour of P. Consequently in order to know what the two colours O and P will be when in juxtaposition, it will be sufficient to find the complementary colour of P and add it to the colour O, and the complementary colour of O and add it to P.

14. An analogous result would be obtained by taking the colour P from O, and O from P.

15. Let us represent

The colour of the stripe O by a, more white by B.
The colour of the stripe P by a', more white by B′.
The complementary colour of a by c.
The complementary colour of a' by c'.

Considered according to the first manner of seeing them (13), the colours of the two stripes seen separately will be:

$$\text{Colour of O} = a + \text{B}.$$
$$\text{Colour of P} = a' + \text{B}'.$$

They will become by juxtaposition as follows;

$$\text{Colour of O} = a + \text{B} + c'.$$
$$\text{Colour of P} = a' + \text{B}' + c.$$

According to the second method of seeing them (14) we suppose

$$\text{B reduced to two portions} = \begin{cases} \text{white} = b. \\ + \text{ white} = (a' + c'). \end{cases}$$

$$\text{B}' \text{ reduced to two portions} = \begin{cases} \text{white} = b' \\ + \text{ white} = (a + c). \end{cases}$$

The colours of the two stripes seen separately will be:

$$\text{Colour of O} = a + b + a' + c'$$
$$\text{Colour of P} = a' + b' + a + c;$$

They will become by juxtaposition as follows:

$$\text{Colour of O} = a + b + c'$$
$$\text{Colour of P} = a' + b' + c.$$

The results are the same excepting that there is less white in this case than in the other.

ARTICLE III.—*Application of the Law to the seventeen Observations of Article I.*

Orange and green.

16. Blue (the complementary colour to orange) on being added to green makes the latter incline towards a bluish tint, or renders it less yellow.

Red (the complementary colour to green) when added to orange makes the latter incline towards a reddish tint, or makes it less yellow.

Orange and indigo.

17. Blue (the complementary colour to orange) when added to indigo makes it incline towards a blue tint, or renders it less red.

Yellow inclining to orange (the complementary colour to indigo) makes orange incline towards yellow, or makes it less red.

Orange and violet.

18. Blue (the complementary colour to orange) makes violet incline towards indigo.

Yellow inclining towards green (the complementary colour to violet) makes orange incline towards a yellow tone of colour.

Green and indigo.

19. Red (the complementary colour to green) when added to indigo renders it more violet, or more red.

Yellow inclining to orange (the complementary colour to indigo) on being added to green causes it to incline towards yellow.

Green and violet.

20. Red (the complementary colour to green) on being added to violet gives it a redder tinge.

Yellow inclining to green (the complementary colour to violet) on being added to green makes it incline to yellow.

Orange and red.

21. Blue (the complementary colour to orange) on being added to red makes it incline towards violet.

Green (the complementary colour to red) makes orange incline towards yellow.

Violet and red.

22. Yellow inclining to green (the complementary colour to violet) on being added to red makes it incline to orange.

Green (the complementary colour to red) causes violet to incline towards indigo.

Indigo and red.

23. Yellow inclining to orange (the complementary colour to indigo) on being added to red, causes it to incline towards orange.

Green (the complementary colour to red) makes indigo incline to blue.

Orange and yellow.

24. Blue (the complementary colour to orange) makes yellow incline to green.

Indigo inclining to violet (the complementary colour to yellow) give a reddish tinge to orange.

Green and yellow.

25. Red (the complementary colour to green) on being added to yellow makes it incline to orange.

Indigo inclining to violet (the complementary colour to yellow) makes green incline towards blue.

Green and blue.

26. Red (the complementary colour to green) on being added to blue makes it incline towards indigo.

Orange (the complementary colour to blue) on being added to green makes it incline towards yellow.

Violet and blue.

27. Yellow inclining to green (the complementary colour to violet) makes blue incline to green.

Orange (the complementary colour to blue) on being added to violet makes it incline to red.

Indigo and blue.

28. Yellow inclining to orange (the complementary colour to indigo) on being added to blue makes it incline to green,

Orange (the complementary colour to blue) on being added to indigo makes it incline to violet.

Red and yellow.

29. Green (the complementary colour to red) on being added to yellow makes it incline to green.

Indigo inclining to violet (the complementary colour to yellow) makes red incline to violet.

Red and blue.

30. Green (the complementary colour to red) on being added to blue makes it incline towards green.

Orange (the complementary colour to blue) on being added to red makes it incline towards orange.

Yellow and blue.

31. Indigo inclining to violet (the complementary colour to an orange yellow) makes blue incline towards indigo.

Orange (the complementary colour to blue) makes yellow incline towards orange.

Indigo and violet.

32. Yellow inclining to orange (the complementary colour to indigo) on being added to violet makes it incline towards red.

Yellow inclining to green (the complementary colour to violet) on being added to indigo makes it incline towards blue.

33. It is evident that, other things being the same, the modification of colours in juxtaposition will be more marked in proportion to the difference between the complementary colours (c or c') added to each; for supposing that the complementary colour c' added to O be identical with it, as would be the case with the complementary colour c added to the colour P, the modifications of O and P would be confined to a mere augmentation in the intensity of the colour. But do we know at the present day any two coloured bodies capable of presenting to our view two perfectly pure colours complementary to each other? Assuredly not. All that we observe coloured by reflection transmit, as I have already remarked (5), besides white light, a great number of differently coloured rays. We are not, therefore, able at present to name a red body and a green body, or an orange body and a blue body, or a body of a yellow inclining to orange and an indigo-coloured body, or, finally, a body of a yellow inclining to green and a violet-coloured body, reflecting colours that are perfectly pure and complementary to each other, so that their juxtaposition shall merely occasion a *simple augmentation of intensity in colour*. If, therefore, it be less easy in general to verify the law of contrast with respect to *red and green bodies, or orange-coloured and blue bodies, &c.*, than with reference to those of which I have treated in the seventeen observations, detailed at (10), we shall find that, in endeavouring to establish this law for the first-named bodies, their colours will acquire the most remarkable splendour, vivacity, and purity, and this result, which is perfectly conformable to the law, will be easily understood, since any object, for instance, of an orange colour reflects blue rays in the same manner as an object of a blue colour reflects orange rays (5). Thus, it is evident that when you place a blue stripe in contact with one of an orange colour, the colours of the two objects in juxtaposition will be mutually purified and rendered more brilliant, whether this arise from the first-named stripe imbibing blue from the vicinity of the second, as that again receives orange from the vicinity of the blue stripe (13), or whether we assume that the blue stripe

destroys the effect of the blue rays of the second stripe, as that destroys the effect of the orange rays coming from the blue stripe (14). It may, however, happen that the blue appears to incline to green or violet, and the orange to yellow or red, that is to say, that the modification is not limited to intensity of colour, but extends likewise to the physical composition; whatever the case may be, if the latter effect be produced, it will incontestibly be much more feeble than the former, and furthermore, on looking a certain number of times at the same coloured stripes, you will observe that the blue, which at first appeared more green, will soon appear more violet, and that the orange, which had at first seemed to be more yellow, will soon appear to be more red, so that the phenomenon of modification, which depends upon the physical composition of the colour, will not be so constant as those which are treated of in the seventeen preceding observations (10).

I will, however, detail the observations that I have made upon bodies whose colours are nearly complementary to each other.

Red and green.

34. Red (the complementary colour to green) on being added to red increases its intensity.

Green (the complementary colour to red) on being added to green increases its intensity.

Such is the theoretical result.

The practical result is generally in conformity with it, when a green inclining to yellow is brought in juxtaposition with:

1. A red inclining to orange.
2. A crimson red.
3. An intermediate red.

In repeating these observations upon each of these assemblages of colour a certain number of times, different results might be noticed, that is to say, in one case, the red may appear more orange, and the green more yellow, and in another, the red may appear more violet, and the green more blue, and here it may be observed, that this change may be attributed sometimes to a difference in the intensity of the light shining upon the colours, and sometimes, again, to fatigue of the eyes.

On bringing a green of a less yellow or more blue character in juxtaposition with:

1. A red inclining to orange,
2. A crimson red,
3. An intermediate red,

the results will be the same as in the case of the first green, with this difference, however, that in the blending of the blue, green, and the crimson red, when observed a certain number of times, the green and the red will appear almost constantly more yellow than they are separately, a result which may easily be conceived.

Orange and blue.

35. Blue, (the complementary colour to orange,) on being added to blue, increases its intensity.

Orange, (the complementary colour to blue,) on being added to orange,) increases its intensity.

On repeating these experiments with a deep blue and an orange, which is not too red, the two colours will appear most frequently to assume a reddish tinge, otherwise one might observe the contrary.

Yellow, inclining to orange, and indigo.

36. Yellow, inclining to orange, (the complementary colour to indigo,) adds intensity to a yellow inclining to orange.

Indigo (the complementary colour to yellow inclining to orange,) adds intensity to indigo when added to it.

The results of observation and theory are almost invariably in accordance with one another.

37. Yellow, inclining to green, (the complementary colour to violet,) on being added to the same colour gives it intensity.

Violet (the complementary colour to yellow inclining to green,) gives intensity to violet when added to it.

The result of the experiment is almost always in conformity with the law.

Article IV.—*Of the Effect of Colours upon White, and reciprocally of White upon Colours.*

38. If the law, which I have already established, be correct, it will be understood that white itself will be affected by the presence of colours; thus if you bring a colour *o* in juxta-

position with white, the latter will appear slightly coloured by the complementary colour to *o*, although it must be owned that the colour is too feeble to be determined with complete certainty. I have, therefore, contented myself with observing if the colour complementary to the colour used in the experiment corresponded with the tint as seen by my eyes upon the white stripe opposed to the coloured one.

Red and white.

39. Green (the complementary colour to red,) blends with the white.

Red appears more brilliant and deeper.

Orange and white.

40. Blue (the complementary colour to orange,) blends with the white.

Orange appears more brilliant, and of a deeper colour.

Yellow inclining to green, and white.

41. Violet (the complementary colour to yellow inclining to green,) blends with white.

Yellow appears more brilliant and deeper.

Green and white.

42. Red (the complementary colour to green,) blends with white.

Green appears more brilliant and deeper.

Blue and white.

43. Orange (the complementary colour to blue,) blends with white.

Blue appears more brilliant, deeper, and perhaps more green.

Indigo and white.

44. Yellow, inclining to orange, (the complementary colour to indigo,) blends with white.

Indigo appears more brilliant and deeper.

Violet and white.

45. Yellow, inclining to green, (the complementary colour to violet,) blends with white.

Violet appears more brilliant and deeper.

Black and white.

46. Black and white, which may, in some degree, be considered as complementary to each other become, conformably to the law, more different from each other than when seen sepa-

rately, and this is owing to the effect of the white light reflected by the black, being more or less destroyed by the light of the white band. By an analogous action white heightens the tone of the colours with which it is brought in juxtaposition.

Article V.—*Of the Effect of Colours upon Black, and reciprocally of Black upon Colours.*

47. The phenomena presented by black, when exposed to the influence of colours, appears to me to be owing to the colour with which it is brought in contact, acting, relatively to the eye, upon the white light reflected by the black surface in the same manner as if it were brought in juxtaposition with a white surface. According to this, the black should be tinged by the complementary tone of the colour touching it, and as the tinge which it assumes is not weakened by so much white light, as in the case where the colour is brought in contact with white, it must to be so much the more striking. On the other hand, as white heightens the tone of colours brought in contact with it, black, on the contrary, tends to make them lighter. The tone of black must depend (1) upon the colour added to it; thus, for instance, an orange-coloured red, an orange-coloured yellow, or a yellowish green, will brighten it, whilst indigo, even if it does not heighten the tone, will at any rate not reduce it as the first-named colours. (2) Upon the force or brilliancy of the colour in juxtaposition with it; thus bright colours, like orange and yellow, will tend by their brilliancy to add force to black, whilst sombre colours, such as blue and indigo, do not produce a similar effect.

Red and black.

48. Green (the complementary colour to red,) blends with black, and makes it appear less reddish.

The red becomes more brilliant, and has less of an orange or brown tone of colour.

Orange and black.

49. Blue (the complementary colour to orange,) blends with black, and makes it appear less red or more blue.

The orange becomes brighter and yellower, or less brownish.

Yellow, inclining to green and black.

50. Violet (the complementary colour to a greenish yel-

low,) blends with black, and the latter then acquires a violet-coloured hue.

The yellow appears brighter, more greenish, or lighter.

Green and black.

51. Red (the complementary colour to green,) blends with black, rendering it more violet or reddish.

The green inclines slightly to yellow.

Blue and black.

52. Orange (the complementary colour to blue,) blends with black, and brightens it.

The blue inclines slightly to green.

Indigo and black.

53. Yellow, inclining to orange, (the complementary colour to indigo,) blends with black, and brightens it considerably.

The indigo becomes brighter.

Violet and black.

54. Yellow, inclining to green, (the complementary colour to violet,) blends with black, and brightens it.

The violet becomes more brilliant, lighter, and redder.

Article VI.—*Upon the Influence of the Chemical nature of coloured Bodies upon the Phenomena observed.*

55. It is necessary to examine into the influence exercised by the chemical nature of coloured bodies in juxtaposition on their reciprocal modifications. The result at which I have arrived is, that all the above-named modifications occur, let the chemical nature of the coloured bodies in juxtaposition be what it may, provided always, that the coloured substances that are substituted for one another, are identical in colour.

Example.—The results were the same in using indigo for Prussian blue or ultramarine; likewise in substituting stripes of orange coloured with minium for stripes coloured with anotto or with woad-yellow reddened either by madder or cochineal.

Article VII.—*On the Reciprocal Influence of different kinds of Colours appertaining to the same Group.*

56. Whenever a great difference is produced by the juxtaposition of two colours, it is rendered appreciable by bringing

the same colour successively in contact with the various colours belonging to one group, for example:

1. Red and orange.

57. On placing a scarlet, or a crimson red in contact with an orange, the red will invariably acquire a purple, and the orange a yellow tone of colour.

2. Red and violet.

58. Analogous results are obtained on bringing a scarlet and crimson red in contact with violet. The latter will appear to be bluer, and the red more yellow or less purple.

59. These observations will clearly explain the cause of our obtaining results conformable to the formula, notwithstanding that colours or papers may have been used far from presenting to the eye any very true colours.

60. The juxtaposition of coloured stripes affords a means of demonstrating the difficulty of fixing the type of colours, thus:

1. On taking red and bringing it in contact with an orange-coloured red, the former will appear purple and the latter more yellow, as I have already remarked; but on placing the first-named red in contact with a purple red, the latter will become more blue, and the former more yellow or orange, so that the same red will be purple in one case and orange in the other.

2. On taking yellow and putting it in juxtaposition with an orange-coloured yellow, the former will appear greenish and the latter more red; but again, on bringing the first-named yellow in contact with a greenish yellow, the latter will appear greener and the former more orange, so that the same colour will, in one case, incline to green and in another to orange.

3. On taking blue and placing it in contact with greenish blue, the former will incline to violet, and the latter will appear more yellow. If the same blue be brought in contact with a violet blue, the former will incline to green and the latter will appear more red; so that the same blue will have a violet tinge in one case, and a greenish hue in the other.

61. We thus see that those colours which are termed by

painters simple or primitive, as red, yellow, and blue, insensibly pass by the effect of juxtaposition into the condition of compound colours, the same red becoming purple or orange, the same yellow orange or green, and the same blue appearing either to be green or violet.

ARTICLE VIII.—*On the Interpretation of these Phenomena on the Hypothesis that Red, Yellow, and Blue are Simple Colours, and Orange, Green, Indigo, and Violet are Compound Colours.*

62. The instances in which I have applied the principle of the modification that colours experience by juxtaposition, and the explanation resulting from the manner in which we consider the composition of white light physically, are further elucidated by the terms adopted by painters and dyers, who only admit of three primitive colours, red, yellow, and blue. As there may be many who entertain the same opinion, but who might, nevertheless, wish to understand the phenomena resulting from the juxtaposition of colours, I will proceed to give an explanation of them, conforming to the terms commonly used; and, for the sake of perspicuity, I purpose dividing the whole into five groups, beginning with those which comprehend the observations to which the above-named law most readily applies. I will suppose, then, that orange is formed of red and yellow, green of yellow and blue, and indigo and violet of blue and red.

First Group. Two compound colours having a simple colour as their common element.

It is very easy to verify the law by observing two colours comprehended in this group: we perceive that, owing to their reciprocal influence, they lose more or less of the colour common to both; and it is therefore evident that the degree in which they differ will be proportionate to the amount of this loss.

1. Orange and green.

These two colours, which have yellow as a common element, lose it by juxtaposition, thus: *the orange will appear more red and the green more blue.*

2. Orange and indigo.

These two colours, which have red as their common element, lose it by juxtaposition: *the orange appearing more yellow and the indigo more blue.*

3. Orange and violet.

As the preceding.

4. Green and indigo.

These two colours, which have blue as their common element, lose it by juxtaposition: *the green appearing yellower and the indigo redder.*

5. Green and violet.

Like the preceding.

Second Group. A compound colour, composed of one simple and one compound colour.

1. Orange and red.

The orange loses its redness and appears yellower, and the red becomes more blue, differing as much as possible from orange.

2. Violet and red.

Violet loses its redness and appears more blue, the red becomes yellow, differing as much as possible from violet.

3. Indigo and red.

Like the preceding.

4. Orange and yellow.

Orange loses its yellow tinge and becomes redder, red becomes more blue, differing as much as possible from orange.

5. Green and yellow.

Green loses its yellow tinge and appears more blue, the yellow becomes red, differing as much as possible from green.

6. Green and blue.

Green loses its blue tinge and becomes yellower, the blue becomes red, differing as much as possible from green.

7. Violet and blue.

Violet loses its blue tinge and appears redder, the blue becomes yellow, differing as much as possible from violet.

8. Indigo and blue.

Like the preceding.

Third Group. Two simple colours.

1. Red and yellow.

Red, on losing yellow, will appear more blue, and yellow, on

losing red, will appear more blue; or, in other words, the *red inclines to purple and the yellow to green.*

2. Red and blue.

Red, on losing blue, will appear yellower, and blue, on losing red, will appear yellower; or, in other words, the *red inclines to orange and the blue to green.*

3. Yellow and blue.

Yellow, on losing its blue, will appear redder, and blue, on losing yellow, will appear more violet; or, in other words, the *yellow inclines to orange and the blue to violet.*

Fourth Group. Two compound colours having the same simple colours.

Indigo and violet.

As indigo only differs from violet in containing a larger proportion of blue in comparison with the red, it follows that the difference will be very considerably increased by the indigo losing red and inclining to a greenish blue, whilst the violet, acquiring more red, will incline to that colour. It is evident that if the violet lost its red, or the indigo gained more red, the two colours would approximate; but as they vary from one another the first-named effect will be produced.

We may further explain this phenomenon by considering indigo relatively to violet as blue; thus it will lose its blue, that being common to both colours, and will incline to green.

Fifth Group. A compound colour and a simple colour which does not occur in it.

If we adopt the hypothesis that orange, green, indigo, and violet are compound, and red, blue, and yellow simple colours, it necessarily follows, that, on bringing one of the four compound colours (supposed to be perfectly free from any admixture with a colour foreign to its two elementary colours) in contact with one of the three simple colours not comprised in its composition, we do not see any reason, by which to explain the loss sustained by the compound colour of one, rather than of another of its elementary colours, and why the simple colour should be removed from one rather than another of the elementary colours. For instance, on placing green in contact with red, there seems no reason that the green should tend towards blue rather than yellow, or why the red should incline to blue rather than to yellow.

ARTICLE IX.—*On the connection existing between my Observations and those previously made by Natural Philosophers.*

63. Buffon* was the first who described, under the name of accidental colours, several phenomena of vision, which, according to his explanation, are all so far analogous, that *they result from too great vibration, or from fatigue of the eye,* differing in this respect from the colours under which those bodies appear, which are coloured in a constant manner, whether they decompose light by acting upon it by *reflection, refraction,* or *inflection.*

64. Accidental colours may arise from different causes; for example, they may be perceived under the following circumstances.

1. When the eye is compressed in the dark:
2. In consequence of a blow on the eye:
3. When the eyes are closed after having been for a moment fixed upon the sun:
4. When the eyes are fixed upon a small square piece of coloured paper laid on a white ground; if the square be red it will appear bordered by a faint green; if yellow it will be bordered by blue; if green by a purplish white; if blue by a reddish white; and if black by a vivid white:
5. If, after having observed the preceding phenomena for a considerable time, we turn our eyes to the white ground in such a manner as no longer to see the small square of coloured paper, we shall perceive a square of an extent equal to the former, and of the same colour as that which bordered the small square in the preceding experiment (4).

65. I could cite many other instances in which *accidental colours* are produced, if I did not fear departing too far from the principal object I had in view in my memoir, which was to give an exposition of the *law regulating the modifications mutually experienced by differently coloured bodies in juxtaposition and when seen simultaneously;* before proceeding further, I must, however, direct particular attention to the distinction of the two cir-

* See *Mémoires de l'Académie des Sciences,* 1743.

cumstances, 4 and 5, in which Buffon observed accidental colours.

66. I trust that I shall be able to prove, by means of the details into which I am about to enter, that, owing to this want of attention, one of the subjects of optics admitting of the most comprehensive application has not generally been treated with the precision and clearness necessary to exhibit its importance to those who, without having made any observations upon the subject, have confined themselves to a mere perusal of what has been written upon it. This distinction is further necessary for the appreciation of the new facts that my researches have added to the history of vision: I will designate by the term *simultaneous contrast* the modification of colour and height of tone experienced by two differently coloured objects when seen simultaneously; by way of opposition, I will apply the term *successive contrast* to the phenomena observed when the eyes, after having looked for a certain time at one or more coloured objects, perceive images of a colour complementary to that which appertains to each of these objects. It is doubtless superfluous to remark that the fourth instance above-mentioned appertains to a *simultaneous contrast*, whilst the fifth refers to a *successive contrast*. I shall notice the principal works and experiments instituted with reference to accidental colours.

67. Father Scherffer, in 1754, laid much stress upon the phenomena appertaining to a *successive contrast*, demonstrating that a given colour produced an accidental colour, that, namely, which we now call its *complementary* colour, and by this law he rectified several observations of Buffon. Not content with this, he sought to explain the cause of the phenomenon, in the manner I shall explain in the following article. He only slightly touched upon a *simultaneous contrast*. (See his memoir, § xv., *Journal de Physique*, t. xxvi.)

68. Æpinus* and Darwin† also turned their attention to a *successive contrast*.

* *Memoires de l'Académie de Pétersbourg et Journal de Physique, année* 1785, t. xxvi., p. 291.

† *Philosophical Transactions*, vol. lxxvi. 1785.

69. Count Rumford* made *simultaneous contrast* an object of experiment and observation (3), and to these researches I must refer, since they are more nearly analogous with my own than any other that have been made upon the subject. It was demonstrated by Count Rumford, after having observed that a shadow in a ray of coloured light, (illumined by a ray of white light of equal intensity with the former,) appeared tinged with the complementary colour of the coloured ray, when it was near a shadow of equal size produced in the white ray illumined by the red ray:

(1.) That the result is the same when the ray of coloured light is replaced by light transmitted through a glass, or any other coloured medium, or by the coloured light reflected by an opaque coloured body.

(2.) That if, in a circle of white paper placed upon a large sheet of paper, lying on the floor of a room, two bands of paper 6 lines in width and 2 inches in length be laid side by side, one being covered with a powder of the colour A, whilst the other is covered with a powder composed of white-lead and lamp-black in such a proportion that the light reflected from this powder is equal in intensity to the coloured light of A, a person looking with one eye through his hand at these two stripes will see the one covered with gray powder tinged by the complementary colour of A, which will be as brilliant as A itself.

The author remarks that, in order to prosecute this experiment successfully, it is necessary to take many precautions, not only to avoid the light reflected from neighbouring objects, but also to procure a gray capable of reflecting a light equal in intensity to the coloured light. He observes that the difficulties are very great if colours be taken that have been ground in oil, owing to the latter giving a brown tinge to these colours, which never retain the purity of the colours of the spectrum.

70. If it be true that the experiments of Rumford correspond to those I have made upon colours in connection with black and white, and that they afford a particular instance

* Experiment upon Coloured Shadows; Conjectures on the Principles of the Harmony of Colours. Rumford's *Philosoph. Papers*, &c., vol. i. London, 1802.

of the law of contrast as I have established it, it is not less so that the law cannot be educed without making the series of experiments which I have prosecuted. For as the experiments of Rumford comprised the maximum of the phenomenon, it could not be affirmed that, under ordinary circumstances, there would be not only a modification of white and black by colours in juxtaposition, but also a modification of the latter. We have actually seen that colours brought in contact with white become deeper, and that they grow fainter when in contact with black, the contrast as I have demonstrated embracing both colour and the height of tone in the colour.

71. Struck by observing in his experiments, that a coloured ray developed its complementary colour, Rumford laid it down as a principle, that *two colours to be in harmony must both present the respective proportions of the coloured light necessary to form white.* And he therefore recommended ribbons destined for the toilet of ladies, and the colours in furniture, to be assorted in accordance with this law. He likewise thinks that painters may derive much benefit from an acquaintance with the principle; it is evident, however, that this law of the harmony of colours proposed by Rumford is nothing more than an ingenious invention of fancy, and that as he laid it down, it could not very easily be made to throw light upon the practice of painting. I shall, however, revert to this point in treating of the applications of my own labours; in the meanwhile I would draw attention to the fact, that Rumford has not made any experiment demonstrating the influence of two colours in juxtaposition, or more generally, of two colours seen simultaneously.

72. M. Prieur, of the *Côte-d'Or,* is the author that has treated most recently of *accidental* colours*. He has turned his attention to these phenomena, under the name of *contrasts,* which exclusively refer to *simultaneous contrast;* for instance, a small stripe of orange paper appears red when laid upon a yellow ground, whilst it will appear yellow upon a red ground: according to the principle laid down by the author, the accidental colour of the stripe must be that resulting from its own colour, without abstracting from it that of the ground. *It seems,* remarks he, *that a certain fatigue of the eye,*

* *Annales de Chimie,* t. liv. p. 5.

whether produced instantaneously by the intensity of the light, or more slowly by the prolonged vision, concurs in producing these appearances. He admits, however, *that excessive fatigue in the organ would occasion a degeneration of the colours belonging to another scale.* And he finally adds, *that the colours termed accidental by Buffon, and on the subject of which Scherffer has given an interesting memoir, belong to the class of contrasts, or at least constantly follow the same law.* It is evident that M. Prieur has not made the distinction of the two kinds of contrasts that I have established above.

73. Haüy presented, in his *Traité de Physique*, a *resumé* of the observations of Buffon, Scherffer, Rumford, and M. Prieur; but, notwithstanding the general clearness of style of the illustrious founder of crystallography, there is an obscurity in the absence of the preceding distinction; and this is especially observable in his account of the explanations previously given of these phenomena.

74. According to what has been said, we see,

1. That those authors that have treated of a contrast of colours, have described two kinds of phenomena, without distinguishing the one from the other:

2. That Scherffer has given the law of successive contrast:

3. That Count Rumford has given the law of the modification experienced in a particular case by a gray band, placed in juxtaposition with a coloured one:

4. That Scherffer first, and subsequently M. Prieur, of the *Côte-d'Or*, with more exactitude, have given the law of the modification experienced by a small extent of white or coloured surface from the different colour of the ground on which it is laid.

75. If, on the one hand, it be true, that in this case we perceive, in the most striking manner, the modification which the colour of the small extent of surface is susceptible of receiving from that of the ground, we cannot, on the other, appreciate the modification experienced in the colour of the ground by that of the small surface, owing to our seeing only half of the phenomenon, and we should be greatly in error were we led to think, that a coloured object cannot be modified

by the colour of another, unless the latter be of infinitely larger extent than the former. The manner in which I have disposed coloured objects in my observations on simultaneous contrast, has enabled me to demonstrate:

1. That it is not indispensably necessary to the modification of the colour of one object by that of another, that the former should be of greater extent than the latter, since my observations have been made upon equal and merely contiguous bands:

2. That one may perfectly judge of the modifications experienced by contiguous bands, in comparing them to those which are not in juxtaposition, a circumstance which enables us to see the phenomenon of simultaneous contrast in the most perfect manner, and to establish its *general law*:

3. That in increasing the number of bands not in contact, or which are placed on either side of those which touch each other, and on standing at a suitable distance for the eye to embrace the two series of bands, we see that the influence of one band is not limited to the next band with which it is in contact, but extended to the second, third, &c., although with continually increasing faintness. *Now this influence at a distance ought to be noted,* in order to have a just idea of the generality of the phenomenon.

ARTICLE X.—*On the Physiological Cause by which the Contrast of Colours may be explained.*

76. Scherffer has advanced a physiological explanation of the successive contrast of colours, which seems satisfactory. It is based upon this proposition, *that if a double impression, of which one is vivid and strong, and the other weak, be produced upon one of the senses, we shall perceive the stronger of the two. This occurs principally when both are of the same kind, or when the powerful action of an object on one of the senses* IS FOLLOWED *by another of the same nature, but infinitely weaker or less violent.* We will now proceed to apply this principle to the explanation of the three following experiments on successive contrast.

First Experiment.—We must look for some time at a small white square placed upon a black ground.

On ceasing to look at this, and turning the eye upon a

black ground, we perceive the image of a square, equal in extent to the white square, but instead of being lighter than the ground it will, on the contrary, be darker.

Explanation.—The part of the retina on which the white light of the square acted at the first part of the experiment, is more fatigued than the remainder of the retina, which has only received a faint impression from the faint rays reflected by the black ground; the eye then being fixed upon the black ground during the latter part of the experiment, the weak light of this ground acts more strongly upon that part of the retina which is still unexhausted, than upon that which has already been fatigued, and hence arises the image of the black square seen by that portion of the eye.

Second Experiment.—We must look for some time at a small blue square on a white ground.

Turning the eye away from this, and fixing it on the white ground, we perceive the image of an orange square.

Explanation.—The part of the retina on which the blue light of the square has acted, in the first case, being more fatigued by this colour than the rest of the retina, it happens, in the latter part of the experiment, that the retina which is fatigued by the blue, is consequently disposed to receive a stronger impression from orange, the complementary colour of blue.

Third Experiment.—The eye must be fixed for some time upon a red square on a yellow ground.

Turning it away, we must then fix it upon a white ground, when we shall see the image of a green square upon a violet-blue ground.

Explanation.—At first the part of the retina with which we see the red is fatigued by that colour, whilst the part with which we see the yellow is equally fatigued by the latter, consequently, in the second part of the experiment, the portion of the retina which received the impression of the red now sees green, the colour complementary to it, whilst the portion with which we have seen the yellow sees the violet-blue, its complementary colour.

77. These three experiments, as well as the explanations referring to them, taken at hazard from the memoir of Scherffer

from amongst many others analogous to them, will suffice, I think, to demonstrate that it was actually the phenomenon of *successive contrast* which specially occupied that ingenious observer. Considering this, it is certainly strange that Haüy, in endeavouring to make known the explanation given by Scherffer, should have spoken exclusively of the case of a *simultaneous contrast*, a phenomenon which the latter naturalist has only casually mentioned, as I have already remarked at 67; for the rest, the following are the words in which Haüy expresses himself on this subject, taking as an illustration the case in which a small stripe of white paper is placed upon red paper; "We may," says he, "consider the whiteness of this stripe as being composed of a bluish green and red. But the sensation of the red colour, acting with much less force than that produced by the surrounding colour of the same kind, is eclipsed by the latter, so that the eye is only sensible of the impression of the green, which being, as it were, foreign to the colour of the ground, acts upon the organ with all its force."

78. Although this explanation appears to be a natural consequence of the principle set forth by Scherffer, the latter does not seem to me to have applied it to the explanation of simultaneous contrast, and the passage quoted above (67) of his memoir is very clear: this must principally take place when they (the impressions) are *both of the same kind, or when the powerful action of an object on one sense is followed by another of the same nature, but infinitely more weak, and less violent.*

79. Let us now see what difference exists between the explanation of *successive contrast*, such as Scherffer has demonstrated it, and that attributed to him by Fenäy in the case of *simultaneous contrast.* All the observations on successive contrast explained by Scherffer present this result, that the portion of the retina, which in the first part of the experiment is struck by a given colour, sees in the subsequent part of the observation the complementary colour to the given colour, and this new impression is independent of the extent of the coloured object relatively to that of the ground on which it is placed, or, to speak more generally, of the objects surrounding the former.

80. This is not expressed in the explanation attributed by Haüy to Scherffer, thus:

1. The portion of the retina that sees the white stripe placed on a red ground sees it as if it were of a bluish green, that is to say, the complementary colour to the ground. Now, according to the experiments of Scherffer, this portion, fatigued by white light, *has a tendency to see not a bluish green, but black*, which is in some degree complementary to white.

2. In order to admit the explanation attributed to Scherffer, it would be necessary that the object, whose colour is modified by that of another, should in general be of much smaller extent than the latter, since it is only by this excess of extent in the modifying body that we can conceive *in general* that excess of action which neutralized a part of that of the first object; I say *in general*, because there are cases, in which it might be said, that a much brighter colour might modify one that was less so, although it might actually occupy a very small space around it. In reverting to what has been said, we shall perceive the difference between the explanation given by Scherffer of *successive contrast* and that attributed to him on simultaneous contrast.

81. If we revert to this last explanation in order to test its force, not under the circumstances related by these authors of a small stripe appearing to be alone modified when seen on a ground, but in the case of two stripes of equal extent being mutually modified, not only when in contact, but at a distance as shown by my observations; we shall readily appreciate the difficulty that presents itself, thus:

Fig. 3.

1. Let us suppose that figure 3 represents the image of a red stripe r contiguous to a blue stripe b, depicted on the retina; the former will acquire yellow or lose blue, and the second will acquire yellow or lose red. Now, it is the portion of the retina on which the image of the stripe r is impressed that will lose its sensibility for red, as it is the part of the retina on which the image of the stripe b is impressed that will lose its sensibility for

blue; consequently, I do not perceive how it can be the part *r*, which in reality loses its sensibility for blue, or how it can be the part *b*, which loses its sensibility for red.

2. In my observations, where the stripes are of equal extent, there seems no reason, as in the case of a small stripe being laid upon a ground of great extent, that one of the stripes should modify the other by the great fatigue each one occasions the retina.

82. It was doubtlessly owing to the difficulties presented by the explanation we have been considering, that the illustrious author of the Mécanique Céleste was led to propose another, which Haüy inserted in his *Traité de Physique* at the end of the one attributed by him to Scherffer: the case is still that of a little stripe of white paper placed upon a red ground. The illustrious geometrician supposes, as Haüy observes, "that there exists in the eye a certain disposition, by means of which the red rays comprised in the whiteness of the small stripe are attracted, as it were, at the moment they reach this organ, by the rays forming the predominating red colour of the ground, so that the two impressions form only one, and that of the green colour is enabled to act as if it were alone. According to this method of understanding the subject, the sensation of the red decomposes that of the whiteness, and whilst the actions of the homogeneous rays unite together, the action of the heterogeneous rays being disengaged from this combination produces its separate effect."

83. I will not contest the truth of this explanation beyond making the remark, that it admits by implication the necessity of the modifying colour occupying a larger extent of surface than the colour modified; it is probable, however, that such an opinion would not have been advanced if the illustrious author had been acquainted with the true explanation of Scherffer on successive contrast, and if instead of citing a single experiment of simultaneous contrast, which does not include more than half the phenomenon, one had been laid before him in which differently coloured stripes of equal extent were seen to modify each other, even when not in contact.

84. After having shown the insufficiency of the explanations that have been given of *simultaneous contrast*, it only

remains for me to speak of the connexion, which appears to me to exist between the organ of vision and the phenomenon, observed under the circumstances in which I have studied it. All the authors who have treated of accidental colours agree in considering them to be the result of fatigue of the eye; if this be incontestably true of *successive contrast*, I do not believe it to be so with reference to simultaneous contrast, for in arranging the coloured stripes in the manner I have done, as soon as we succeed in seeing all four together, the colours may be observed to be modified before the least fatigue is experienced by the eye, although I admit that it frequently requires several seconds before these modifications can be perfectly well recognised. But is not this *time* necessary as the same that we give to the exercise of each of our senses, whenever we wish to give an exact account of the perception of a sensation affecting them? There is, besides, a circumstance that explains in many instances the necessity of *time*. This is the influence of white light reflected by the surface modified, which is sometimes sufficiently strong to weaken the result of the modification; and the greater part of the precautions proposed for seeing the accidental colours of simultaneous contrast are therefore directed towards the diminution of the influence of this white light. It is further owing to this cause that gray and black surfaces contiguous to the surfaces of very bright light colours, as blue, red, and yellow are modified more than a white surface would be by their vicinity. The following is an instance accidentally presented to my observation, and which will afford a good illustration of my idea. A coloured paper, the writing on which had been traced with a pale gray substance, was presented to me one evening at twilight; on first looking at it, I could not trace a single letter, but at the end of a few minutes I contrived to read the writing which appeared to me to have been traced with an ink of a colour complementary to that of the ground. Now, I would ask, if at the moment when my vision was perfect my eyes were more fatigued than when I first looked at the paper without being able to distinguish the letters upon it, and see them of the colour complementary to that of the ground?

85. I conclude definitely from my observations, that whenever the eye simultaneously sees two differently coloured objects,

the analogous character of the sensation of the two colours experiences such a diminution, that the difference existing between them is rendered proportionately more sensible in the simultaneous impression of the two colours upon the retina.

II. Applications.

86. The preceding observations, and the announcement of the law, which by its generalizing character simplifies them so much, will suffice to enable the reader to make all the applications of which they are susceptible, whether in assorting coloured objects for the purpose of producing a definite effect or in judging of the colours of dyed stuffs relatively to their effect upon the eye without regard to their permanency. Among the few examples to which I must limit myself, I will cite the following:

Article I.—*Application to the Art of Weaving coloured Stuffs.*

First Application.—The assortment of coloured threads to imitate the colours of a painting.

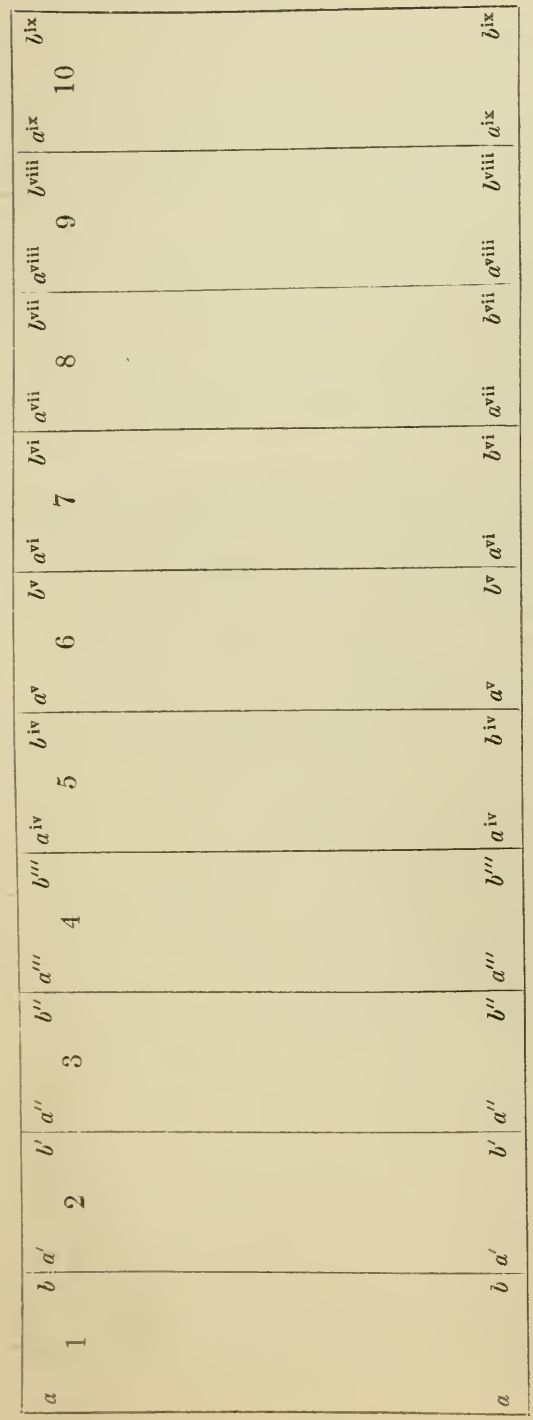
First Example.

87. A painter delineates two coloured stripes in a picture, one being red and the other blue; they are in contact, and, consequently, the phenomenon of the contrast of two colours in juxtaposition would occur, if the painter had not sustained the red contiguous to the blue stripe by blue, and if he had not sustained the blue stripe by placing red or violet near the red stripe.

88. Suppose a weaver desires to imitate the two stripes of which we have spoken; if he be ignorant of the law of the contrast of colours, he will not fail, after choosing wools and silks suitable to the model before him, to make two stripes presenting the phenomenon of contrast, owing to his having selected his wools and silks of only one blue and one red, with the view of imitating the stripes, which the painter has only succeeded in producing from two colours, (each of which the eye regards as homogeneous through its whole extent,) by means of an artifice, which no one would detect who was ignorant of the law of contrast.

89. Suppose that the painter, instead of painting the two stripes in colours that appeared to the eye to be homogeneous, were to form them with a red and blue, that were not blended on their contiguous borders, the colours would certainly in that case contrast. If now the weaver be ignorant of the law of this phenomenon, he would not fail, in his attempt to imitate his model, to blend yellow or orange with the red, and yellow or green with the blue in the parts of the stripes that come in contact, and the result would be, that the contrast would be more or less exaggerated, from the effect of the picture having been imitated by working with homogeneous colours.

Fig. 4.



Second Example.

90. Let a paper, *a b*, fig. 4, divided into 10 equal zones, be first painted with an uniform tone of any colour, for instance, with an uniform tone of Indian ink; let the zones 2, 3, 4, 5, 6, 7, 8, 9, 10, receive a second wash of the same uniform tone; let the zones 3, 4, 5, 6, 7, 8, 9, and 10, receive a third, and so on

until 10 zones be procured, which gradually increase in depth of tone, proceeding from the first onward. The remarkable part of the phenomenon here is, that each zone will present at least two shades, owing to the contrast produced by contiguity; for instance, in beginning from the first, the border *b b* of this zone, contiguous to the border *a′ a′* of zone 2, will appear lighter than the border *a a;* and, consequently, two shades will be presented in zone 1, and the same in the others. But it is possible that a larger number may be distinguished, especially in the intermediate zones between 2 . . . . 9; provided they are of sufficient breadth, and this is owing to the borders *a′ a′ a″ a″*—being lighter, and the borders *b′ b′ b″ b″*—darker than the general tone of the zone, when by reason of contrast, the middle of the zones, being less affected than the borders, will present a third tone of colour. It will be evident that the three tones, or the two tones, as the case may be, presented by the zone, will not terminate abruptly, but blend into one another.

91. Suppose a weaver were to copy the figure we have composed, if he were unacquainted with the effect of the contrast of contiguous zones, he would exaggerate the effect in his work, using probably at least twenty shades of the same colour instead of the ten.

92. These examples convey a better idea than all the reasoning we could enter upon, of the fundamental difference existing between the employment of colours in painting and in weaving. A painter may, to a certain extent, succeed without a knowledge of the law of simultaneous contrast; for if he produce an effect with which he is not satisfied, depending upon this phenomenon, his palette furnishes him with the means of destroying or increasing it. The weaver has not the same resources at his command; he cannot replace his colours without undoing his work, and to avoid this necessity he ought to be sufficiently well acquainted with the law of contrast, to judge of the effect that will be produced by the vicinity of other colours upon the coloured threads he employs in the imitation of a certain part of his pattern, otherwise it will be impossible for him to reproduce a faithful copy of the painting before him.

Second Application.—To work on black with blue and violet.

93. The observations made at Article V. § 1, teach the weaver that there are colours, such as yellow and orange, which may be worked in with black without weakening its intensity, whilst there are others, as blue, indigo, and violet, which produce the contrary effect, by giving it somewhat of a yellow, green, or olive tint. It is consequently necessary to avoid making blue or violet contrast with black, when shadows are to be produced in blue or violet stuffs, and the object required may be obtained by various means, as I am about to indicate.

Article II.—*Application to the Art of Printing Patterns upon Coloured Stuffs or Painted Papers, and Coloured Inks upon Coloured Paper.*

94. In these applications, I exclude the consideration of the chemical action that may exist between the substance of the coloured stuffs or the painted paper, and that of the colouring matter used, confining myself to the optical effect.

95. I have frequently been appealed to as an arbiter in cases where persons having given to be printed various woollen stuffs for furniture and ladies' cloaks, have had disputes with the printer on the subject of the patterns, which were not of the colour intended. I have often found that these complaints depended upon the effect of the contrast of the colour of the designs with that of the ground, and that if the printer were reprehensible, it was not for having printed a different colour from the one required, but for not having foreseen the effect that would result from the contrast of colours, one of which was to serve as a ground for another.

Examples.

1. When black patterns are printed upon red, crimson, or amaranth grounds they appear green, owing to green, the complementary to the ground, blending with the black (48).

2. For the same reason, black, when printed on violet stuffs, or on dark green, loses all its force.

96. The method I have adopted in the cases in which I

have been appealed to as an arbiter, was, by a simple process, to prove that the designs which did not appear black were actually so, and it consisted in cutting a piece of white paper in such a manner as to cover the ground and only show the pattern.

97. Similar difficulties have presented themselves in manufactories of paper-hangings, when it was required to produce a design of a slightly yellowish-gray upon a green ground. These designs, although actually gray, appeared, when once printed, to be pink, owing to the complementary colour of the ground. If they had been on a rose-coloured ground they would have appeared green, for the same reason.

98. Finally, in wishing to impress letters upon coloured paper, the rule to be followed is to choose a ground that is of the colour complementary to that of the ink. Thus, we must use violet-coloured ink for a yellow paper, and yellow ink on a violet-coloured paper; red ink on green paper, and green ink on red paper; orange-coloured ink on blue paper, and blue ink on orange-coloured paper.

Article III.—*Application to the Assortment of Stuffs with the Woods employed in Upholstery.*

99. Amongst the numerous applications of the law of simultaneous contrast to the art of the upholsterer and house decorator, there is one to which I shall call attention, since it is too often disregarded, I allude to the assortment of stuffs with the fancy woods used in upholstery, for making easy chairs, sofas, &c. The principle to be followed in making the most effective assortment is to choose *violet or blue stuffs for yellow woods, as orange-wood, the root of the ash, &c.; and green or yellow stuffs for red woods, like mahogany.* The colour of the stuff must be as different as possible from that of the wood.

100. Many persons prefer, even for mahogany, to have a crimson stuff, owing to its being one of the best colours for standing light. Although this assortment is contrary to principle, the bad effect admits of being diminished by placing a broad green or black border, either a cord or a printed band, between the crimson and the mahogany. The upholsterer

often borders crimson either with a gold cord or band, fastened on with gold-headed nails, or with yellow silk cord; and these borders, although not complementary, have, at any rate, the advantage of pleasing many by their brilliancy. There is one assortment, however, which ought never to be made, namely, that of yellowish red, as scarlet, flame-coloured, or light-red stuffs with mahogany; since their brightness is such that they deprive the wood of that red colour which constitutes its beauty, and makes it resemble oak or walnut.

Article IV.—*Applications to the Painting of Pictures in general, and to the Patterns of Woven Stuffs, and of Carpets in particular.*

101. There are, as is well known, two systems of painting, that of plain tinting and of *chiaro-obscuro.* In the former, the colours are not shaded, nor blended in one another, nor modified by reflections, as in the second. Perspective is reduced in these kind of paintings to an observation of mere linear perspective, and to the employment of vivid colours for the first coat, and pale or gray colours for the last. If the choice of the contiguous colours have been made in conformity with the law of simultaneous contrast, the effect of the colouring will be more striking than where the painting has been done according to the system of chiaro-obscuro. In admiring the beauty of the colours of those plain-tinted paintings, which we receive from China, we ought, in comparing them with our own, to take into account the system by which they have been done, otherwise we might form an erroneous judgment in comparing pictures that have been painted according to such different systems.

102. If the system of plain tinting is more favourable to show the brightness of the colours used, it ought to be a motive for the painter who follows the system of chiaro-obscuro to make himself thoroughly conversant with the resources held out to him by the application of the law of simultaneous contrast. He ought to multiply his draperies of different colours as much as his subject allows of it, and if he cannot, he ought to bring out his colours by well-chosen and skilfully-

handled reflexions: thus, for instance, green or yellow reflexions bring out a blue drapery; yellow or orange reflexions bring out a purple and violet drapery; purple reflexions bring out a scarlet drapery. He will give effect to the freshness of flesh colours by avoiding the contact of yellow or orange draperies, as well as grounds of the same colours. He must likewise avoid the fault common to decorative painters of using pink or a light amaranth for the hangings of boxes in a theatre, since these colours have the serious disadvantage of giving a greenish tinge to the complexion.

103. Before entering upon the qualifications which ought to be possessed by the patterns for hangings and carpets, in order to insure the copies approaching as nearly as possible to perfection, we must treat of the special points appertaining to this species of labour. The weaver imitates objects with coloured threads of a certain diameter. These threads passed round the threads of the chain of the warp exhibit not a smooth surface, but one that is furrowed with lines, some running parallel with the warp and deeper than the others which are perpendicular to them; the effect of these furrows is the same that would be produced in a picture by a system of obscure lines intersecting each other at right angles. There are, therefore, the following differences between a piece of weaving and a picture:—1st. That the former never presents the same fusion of colours that the painter can so easily obtain by blending or dividing his colours by means of a more or less viscid solvent. 2nd. That the symmetry and uniformity of the furrows in the weaving are unfavourable to the production of these brilliant lights and effective shadows exhibited by the painter, for while the furrows darken the lights, the salient parts of the threads, which are in the shadows, have the disadvantage of weakening them by the light which they reflect. Add to this, that the painter has other resources denied to the weaver for augmenting the brilliancy of his lights and adding force to his shadows: as, for instance, by the opposition of opaque and glazed colours. He modifies an object of an uniform colour by varying the thickness of the coat of paint laid on the canvas, as well as by the direction in which he lays on the brush. If it were possible to compose a piece of mosaic with such loose elements as the

threads used in the manufacturing of the Gobelin tapestry, a work of the kind would rank between an oil painting and tapestry, resembling the latter, owing to it having resulted from the juxtaposition of coloured elements of an appreciable extent of surface, and approximating to the picture by its smooth surface, which is rendered brilliant by polish; besides the opposition of opaque and transparent elements calls to mind the contrast presented in a picture by the use of opaque and glazed colours.

104. From this state of things, I conclude that, in order to raise tapestry as nearly as possible to painting, it is necessary, 1. That it should represent objects of such a size, that the point where the spectator must stand in order to see them well, should not admit of his distinguishing the coloured elements from one another, nor the furrowed lines separating them; 2. That the colours should be as bright as possible, presenting the strongest contrasts.

105. It is evident, therefore, that the patterns for tapestry should not only be correct in design, and represent elegant forms, but they should be composed of large objects, draped rather than naked, with the dress covered with ornaments rather than simple and uniform; and, finally, that the colours should be varied and bright, presenting the strongest possible contrasts.

106. Although the rules given are applicable in many points to tapestry for furniture and to the patterns for carpets, it may not be wholly useless to make a few remarks relatively to the choice of colours, to the number of tones of the same scale that may be used, and to the choice of the subjects to be represented.

107. For the choice of patterns for damasks (tapestry) for furniture, opposition of the grounds with the predominating colour of the designs upon them is too often disregarded; for instance, where a wreath of flowers is to be represented on a crimson ground, the greater part ought to be composed of blue, yellow, and white flowers; if red flowers are introduced, they should border on orange rather than purple; whilst green leaves laid directly on the ground conduce very considerably to the beauty of the whole; where the ground is green or

dead leaf, the predominating flowers ought, on the contrary, to be pink and red.

108. In the pattern for a *Savonnerie* carpet, the size of the figures ought to be in proportion with the exent of the whole; attention must also be paid to the pattern on the parts concealed by the furniture, so that a figure or any other object composed of different parts, (distinct with respect to design and colour,) may be presented to the eye of the spectator in all its details when the carpet is laid down. In a large carpet, or in one of only middling size, the figures and designs should not be too large, nor should the divisions of one uniform colour cover too large a surface. In a carpet of small extent the designs of the Persian and Turkey carpets are preferable to those which look more like a *picture;* and here we may as well draw attention to the effect produced by palms, straight or waving zones, Vandyck scallops, &c., in which yellow is contrasted with violet, orange with blue, and red with green.

109. Finally, in the case of patterns for tapestry and carpets, where no attempt is made to compete with the effect produced in tapestry or furniture-hangings of the Beauvais style, or in carpets of the Savonnerie manufacture, a scale composed of only four or five tones of colour will be sufficient to give a very good effect, provided the choice of the contiguous colours has been judiciously made.

Article V.—*Applications to Coloured Glass in Gothic Churches.*

110. We will now consider the preceding reflections with reference to coloured glass, which combines so powerfully with the architecture in imparting to large Gothic churches the harmony that cannot fail to strike every one who enters these vast edifices, after having admired the boldness and variety of their external decorations; and which contributes to place these erections foremost among works of art, alike by their grandeur, the subordination of their different parts, and their intimate relation to the purposes, for which they were intended. The coloured glass of Gothic churches produces a strikingly brilliant effect by intercepting the white light, and transmitting

coloured rays, which are less glaring, and more in accordance with the character of the place. If we were to seek for the cause of this effect we should find that it depended not only upon the happy contrast of colours displayed, but also upon the contrast of their transparency with the opacity of the walls around, and of the leaden frames enclosing them. The impressions produced upon the eye, owing to this double cause increase in intensity the oftener and the longer they are examined.

111. The windows in a Gothic church are generally either circular, or pointed towards the top and with vertical sides. The panes in the former usually represent large medallions (roses), in which the yellow, violet, blue, orange, red, and green, seem to sparkle as if from the finest precious stones. The panes of the latter almost always represent, in the centre of a border, or on a ground corresponding with the medallion (rose) windows, a figure of a Saint perfectly in harmony with the figures in alto-relief round the entrances of the church; and these centre figures ought to be judged as *parts of a whole*, and not like a Greek statue intended to be seen isolated from every side.

112. The glass used in composing the different parts of a human figure is of two kinds; either *painted on the surface with colours that have subsequently been glazed; or has the colouring matter fused in with it;* the former is generally used in the composition of the naked parts of the figure, as the face, hands, and feet, whilst the latter composes the drapery; the various pieces of glass are joined together by a leaden frame. I have been most particularly struck in the best specimen of these panes representing the human figure, by the accurate observance of the proper relation of the size of the figures and the intensity of the light to which they are exposed, to the distance at which the spectator is placed, and which is so great that the leaden plates enclosing each square of glass appear like a narrow black circle, or a mere line.

113. It is not necessary to the effect of the whole, that *painted glass* should present, when seen close, delicate touches, careful lining, or much fusion in the colours, for it is intended to be combined with the coloured glass of the draperies in producing a whole, on the system of plain tinting, and it

cannot be doubted that a painting on glass, executed in exact accordance with the rules of chiaro-obscuro, would, to say nothing of the expense of the execution of the work, have this disadvantage, that, the finish of the detail would be wholly lost at the distance of the spectator, and that the whole would appear less distinct: *the first condition to be fulfilled by every object of art intended to attract the eye is, that it should appear as distinct and as clear as possible.* Add to this, that paintings on glass done according to the rules of chiaro-obscuro, are never represented with those borders or grounds of rose or medallion-formed panes (111), which produce such a beautiful effect; that they are less brilliant and less clear than the glass, in which the colouring matter has been incorporated by means of fusion by heat (112), and, finally, that they are less able to resist the effect of time and weather.

114. Variety in the colours of the panes is so necessary to the production of the best possible effect, that those which represent entirely naked figures, edifices, or in fine, any objects of extent of one uniform colour, are very far inferior, let the execution be ever so perfect with respect to finish and truth of invention, to panes composed of pieces of different colours contrasting well with one another.

115. I infer, therefore, that the causes of the good effect of coloured panes of glass in large Gothic churches, must be referred:

1. To their presenting us with a very simple design, whose different and well circumscribed parts may be seen without confusion at a great distance.

2. To their composition of one totally formed of coloured parts, distributed with a kind of symmetry, and being at the same time forcibly contrasted, not only amongst one another, but also with the opaque parts circumscribing them.

Article VI.—*Application to the Distribution of Flowers in a Garden.*

116. Amongst the pleasures presented to us by the culture of flowering plants, there are few that exceed what we experience from the sight of a multitude of flowers varying in

their colour, form, and size, and in their arrangement upon the stem that supports them. It is probably owing to the admiration bestowed individually upon each, and to the attachment bestowed upon them in consequence of the great care they have required, that care has hitherto not been taken to arrange them in such a manner as to produce the best possible effect upon the eye, not only separately, but collectively. Nothing, therefore, is more common than a defect of proportion observed in the manner in which flowers of the same colour are made to recur in a garden. At one time the eye sees nothing but blue or white, at another it is dazzled by yellow scattered around in profusion; the evil effect of a predominating colour may be further augmented, when the flowers are of approximating, but still different shades of colour. For instance, in the spring we meet with the jonquil of a brilliant yellow, side by side with the pale yellow of the narcissus; in the autumn, the Indian pink may be seen next to the China rose and the aster, and dahlias of different red grouped together, &c. Approximations like these produce upon the eye of a person, accustomed to judge of the effects of the contrast of colours, sensations, that are quite as disagreeable as those experienced by the ear of the musician, when struck by discordant sounds.

117. The principal rule to be observed in the arrangement of flowers, is to place the blue next to the orange, and the violet next to the yellow, whilst red and pink flowers are never seen to greater advantage than when surrounded by verdure, and by white flowers; the latter may also be advantageously dispersed among groups formed of blue and orange and of violet and yellow flowers. For, although a clump of white flowers may produce but little effect when seen apart, it cannot be denied that the same flowers must be considered as indispensable to the adornment of a garden when they are seen suitably distributed amongst groups of flowers, whose colours have been assorted according to the law of contrast; it will be observed by those, who may be desirous of putting in practice the precepts we have been inculcating, that there are periods of the horticultural year, when white flowers are not sufficiently multiplied by cultivation to enable us to derive the greatest possible advantage from the flora of our gardens. I will further add,

that plants, whose flowers are to produce a contrast, should be of the same size, and that in many cases the colour of the sand or gravel composing the ground of the walks or beds of a garden, may be made to conduce to the general effect.

118. In laying down the preceding rules, I do not pretend to assert, that an arrangement of colours, different from those mentioned, may not please the eye; but I mean to say, that in adhering to them, we may always be certain of producing assemblages of colour conformable to good taste, whilst we should not be equally sure of success in making other arrangements. I shall, however, revert to this point.

119. I will reserve for a special article, the consideration of the number of plants in flower at the same time, which admit of being grouped together, and of those details of execution which would here be out of place. I must, however, reply to the objection that might be made, *that the green of the leaves, which serves, as it were, for a ground for the flowers, destroys the effect of the contrast of the latter.* Such, however, is not the case, and to prove this, it is only necessary to fix on a screen of green silk two kinds of flowers conformably to the arrangement of the coloured stripes (Fig. 1 and 2), and to look at them at the distance of some ten paces. This admits of a very simple explanation, for as soon as the eye distinctly and simultaneously sees two colours, the attention is so rivetted, that contiguous objects, especially, when on a receding plane, and where they are of a sombre colour, and present themselves in a confused manner to the sight, produce but a very feeble impression.

Article VII.—*Applications to the Colours of Dress.*

120. Many persons observe the fact, that a uniform composed of cloths of different colours looks well much longer, although worn, than one of only a single colour, even when the cloth of the latter is identical with one of those composing the former. The law of contrast perfectly explains the reason.

121. If we suppose a uniform to be made of cloth of two colours, the one complementary of the other, as red and green, orange and blue, yellow and violet, we shall find that the effect will be most excellent from their mutually heightening one

another; and supposing, further, that they are of equal stability, they will present greater advantages, and appear good in spite of atmospheric agents, longer than any other binary combination of colours.

122. In a blue and yellow uniform, the blue gives to the yellow an orange tint, which greatly heightens its effect notwithstanding its tendency, as a dark colour, to make another colour appear lighter; the yellow imparts in its turn a violet tinge to the blue, which considerably improves its appearance, and if the blue had an unpleasant greenish tinge, it would be neutralized by the yellow.

123. On the other hand, stains will always be less visible on a dress of different colours than on one composed only of a single colour, since there exists in general a greater contrast among the various parts of the first-named dress than between the stain and the adjacent parts, this difference renders the effect of the stain less apparent to the eye.

124. For the same reason a coat, waistcoat, and trowsers of the same colour can only be worn to advantage together when all are new; for as soon as one of them loses its freshness, from having been worn longer than the others, the difference will increase by contrast. For instance, a pair of new black trowsers, worn with a waistcoat of the same colour, which is old and a little rusty, will make the tinge of the latter appear more conspicuous, at the same time that the black of the trowsers will appear more brilliant. White, or even light gray trowsers, would produce a contrary effect. We see from this, how advantageous it is to let soldiers have winter trowsers of a different colour from that of the clothes which they wear during the rest of the year; and we can further understand the advantage there is in wearing white trowsers with a blue, or indeed, generally speaking, with any dark coloured coat.

Article VIII.—*Applications to the opinion we form of the Colours of Dyed Stuffs, setting aside the question of their stability.*

125. In order to judge of the colour of a stuff, with respect to its brilliancy, we must remove it from the vicinity of the colours that might produce an effect of contrast upon it;

but, on the other hand, as we cannot judge of two patterns of stuffs of the same colour except by comparing them together, we must, in order to appreciate them correctly, take into account the phenomenon of contrast that would be manifested, if the two patterns were not absolutely identical with respect to colour and height of tone.

First Application.

126. In the case of two patterns, appertaining to the same colour, as two blues or two reds; if the blue or the red of the patterns compared together, be not identical in the two, we must take into consideration the degree to which the effect of contrast might exaggerate the difference; thus, if one blue be greenish, it will make the other appear less green or more indigo, and even more violet than it really is, and reciprocally, the first will appear more green than it would do when seen separately. The same holds good for reds; if one is more orange than the other, the latter will appear more purple, and the former more orange than they really are.

Second Application.

127. Since the contrast of colours that are not analogous, tends reciprocally to embellish and purify them, it is evident that in wishing to form an accurate opinion of the beauty of the colours in carpets, tapestry, and painting, we must take into account the design and the manner in which the colours are shaded, provided the objects compared together are not the exact representation of the same subject; in fine, all other things being the same, identical and unshaded colours, when disposed in contiguous zones, will appear handsomer than if each were seen separately upon a ground which would only produce one single impression upon the eye. Colours arranged in palms, as in the Cachmere shawls, and designs like those of Turkey carpets, produce a more striking effect than if they were shaded, and merged in one another, as is generally the case in paintings. Consequently, if we wished, for instance, to compare the amaranth-coloured zone of an oriental Cachmere with the differently coloured zones on an amaranth ground of a French shawl, we must destroy the contrast of the colours

contiguous to the amaranth zone, by concealing them by means of a gray paper, cut in such a manner as only to show this zone, provided, of course, that a similarly cut paper has been laid over the ground, in order to expose the compared parts to the same influence on the part of the contiguous objects.

128. The same method must be pursued in comparing the colours of old tapestry with new colours, and for this reason: time acts very unequally, not only upon the different sorts of colours applied to stuffs, but likewise upon the tones or shades of the same scale of colour. Thus the dark shades of certain colours fade, as, for instance, the violets in general, while the dark indigo blues, and the dark reds of madder, kermes, and cochineal, stand fast. In the second place, the light tones of the same scale of colour fade in a much shorter time than the darker shades. From hence it follows, that the colours which have resisted the destructive action of time the longest, being more isolated from one another, darker, or less fused, appear on that very account to be more brilliant than if they were otherwise disposed.

Third Application.

129. On looking at the whole of the tones of most of the scales of colour used in the manufacture of tapestries and carpets, the phenomenon of contrast exaggerates the difference observed between the extreme and middle tones of the same scale. Thus, for instance, when all the shades of an indigo blue are seen on silk, the light shades will appear greenish, the browner violet, and the intermediate ones blue. Now the difference of the greenish and violet shades in the extremes, is augmented by the effect of contrast. The same is the case with the yellow scale, the light shades appearing greenish, and the dark ones redder than they are in reality.

Fourth Application.

130. The contrast that increases the difference between black and white, seen simultaneously beside each other, produces an analogous effect upon the different tones of the same scale. This may be deduced from the observation made above (90,) on the subject of the series of 10 zones, which, seen separately,

are of uniform tint, but which cease to appear so when contiguous to one another. Further, the same thing may be directly shown by the following proof. Suppose that in a series of blue tones, designated by the numbers 1, 2, 3, 4, 5, 6, &c., beginning with the light shades, we place the tone 2 between 3 and 4, the blue of 2 will be so much weakened as to appear equal to the tone 1. This result affords a means of judging more accurately than any other, provided the tones of the scale are sufficiently numerous, and at equal distance from one another. In short, if the tone 2, put between 3 and 4, appear equal to 1, it will follow, that if the tones be equidistant, 3, when put between 4 and 5, will appear equal to 2, and 4 between 5 and 6 will appear equal to 3, and so with the rest. If the tones too closely approximate to present this result, they must be successively advanced, not by a single gradation, but by two or three.

131. This method of judging of the equality of distance among tones of the same scale of colour is founded upon the fact, that it is easier to establish an equality of shades than to estimate the distance separating the different tones of one scale, when they are observed in the places which they must occupy according to the respective intensity of their colour.

Resumé, and some general considerations.

132. That which essentially distinguishes the observations I have made in the first part of this memoir from those previously advanced, is the experimental demonstration that two zones of different colours and of the same surface mutually modify each other when seen simultaneously, not only when in juxtaposition, but even when at a distance from one another; and I will add, that these modifications likewise take place on substituting leaves of coloured paper, 20 inches in length and a foot in width, for the bands that have been used in the preceding experiments, the leaves that are used in the experiment being placed at one yard from the contiguous leaves.

133. The law of these modifications being once established we may foresee the changes experienced by any two given colours from juxtaposition, when we know the complementary to each one, and the height of their tone, since the changes

which they experience will result from the complementary to the one being added to the colour of the other, and since, if the two colours be not of the same height of tone, the darker will appear still deeper, as the other will appear lighter than it really is, supposing always that the latter effect is not destroyed by the former.

134. I have drawn attention to the differences existing between the preceding phenomenon, which I have termed *simultaneous contrast,* and the phenomenon I have spoken of as *successive contrast;* in the latter, the same part of the retina which first sees an object under its true colour, sees its image subsequently in the complementary to the true colour; whilst in simultaneous contrast, two different parts of the retina simultaneously see a different object, and see these objects with modifications of colour and of height of tone which would not be presented by them, if one were seen separately from the other.

135. This distinction between the two kinds of contrast throws much light upon the history of the labours undertaken by different natural philosophers on accidental colours. Buffon and Scherffer examined almost exclusively successive contrast; whilst Rumford and Prieur of the Côte d'Or occupied themselves particularly with simultaneous contrast. Haüy, in speaking of the theoretical or explicative portion of accidental colours, has attributed to Scherffer an explanation concerning simultaneous contrast, which does not give an idea of that which the latter Natural Philosopher advanced concerning successive contrast. Finally, Laplace has proposed an explanation of simultaneous contrast, which is not more satisfactory than the preceding one, since it supposes in general that the modifying colour must be of larger extent of surface than the colour modified.

136. Simultaneous contrast, as I have considered it, is a phenomenon of much more frequent occurrence than would be supposed; in speaking of its relation to the organs of vision, I have not pretended to advance a theory, but I have wished to express a fact, which appears to me to be general, *viz.,* that when the eye is *struck* at once by two colours, which it *views with some degree of attention,* the analogous character of these

colours acts less powerfully upon the optic nerve than the heterogeneous; or, in other words, the eye evinces less sensibility in catching the analogies than the differences of the colours, and this without our being able, generally speaking, to say that the organ is fatigued.

137. In the second part of this memoir, I proved, by examples, the number and variety of the applications of the law of *simultaneous contrast;* if some of these might be deduced from what was known of accidental colours independently of my observations, it must be admitted that the majority could not be made without the following propositions having been previously demonstrated: viz., *that two colours seen distinctly and simultaneously are mutually modified, independently of their respective extent, even when they are not in contact, and besides when there is no ground for attributing their modifications to a fatigue of the eye.*

138. After establishing this proposition as a law, and developing its consequences by application, it remains for me to explain the opinion I have given on the system of the harmony of colours advanced by Count Rumford, and which I treated as an invention of fancy, and not as a *demonstrated fact.* It is evident that this observer having remarked that a white light contiguous to a coloured light is tinged by the complementary of the latter, derived from that fact his idea of the harmony of colours, and that he thus implicitly adopted the opinion of those, who, like Darwin, suppose that the beauty of contiguous colours depends upon the relative facility with which the eye distinctly perceives them, and that, consequently, the most beautiful assortments result from opposite colours. I have devoted too much attention to the ideas excited by vision, and to the effect of the arts comprised under its domain, wholly to reject this opinion; but I cannot admit it as a sole and sufficient principle, on which to explain the pleasant or unpleasant sensations produced by such an assemblage of colours, for, in many instances, we cannot deny the influence exercised by the principle of the association of ideas. Whatever it may be, let us then examine the evident facts connected with an assortment of complementary colours and non-complementaries, relatively to the influence which they mutually

exercise in appearing more or less pure, more or less beautiful, without having regard to any systematic view.

Assortment of Complementary Colours.

139. That an assortment of complementary colours is never disagreeable, is a truth that has long been known, but my observations further demonstrate that, *these colours increase in beauty by their approximation to each other, heightening and purifying each other, whatever the difference may be between the different yellow bodies, or the different violet bodies, &c., brought into juxtaposition.* It is, therefore, owing to the fact of our certainty as to the agreeableness of the effect produced by the mutual approximation of complementary colours, not only when pure, but also when a mixture of black and white has rendered them grey, that I have recommended their assortment in preference to every other, for the distribution of flowers in a garden, for stuffs for furniture, uniforms, and liveries; besides this, I have further demonstrated and insisted upon the economy presented by the adoption of these last-named applications.

Assortment of Non-complementary Simple Colours.

140. I am now about to consider the assortment of non-complementary colours, and by way of greater precision, I will begin by speaking of *simple colours*, or more strictly defined, of those which approach the nearest to the seven colours called *primitive.* I will then treat of the assortment of two mixed colours, and of that of one simple and one mixed colour. For the sake of avoiding all unnecessary paraphrase, I will call a colour *mixed*, when it is composed of two or more simple colours.

141. On looking at the arrangements of the coloured zones, which were made the subject of the 17 observations of Article 1, § 1 (10), it must have been made evident, that the *greater part of their tones* which approached as nearly as possible to the seven primitive colours, *increased in beauty as they lost their brown tinge, and acquired more intensity and brilliancy in the same manner as has been observed in the assortment of complementary colours. It was further remarked, that their optical*

composition appeared always, or almost always, to have been more or less changed. So that we may draw from it the following practical conclusion. *If the non-complementary colours which approach most nearly to the seven primitive colours, generally speaking, increase in beauty by their mutual juxtaposition, they nevertheless appear to the eye to have lost more or less of their natural character.*

142. The following are examples of three remarkable cases presented to my observation by these colours.

1. Yellow and blue mutually increased in beauty by juxtaposition, the former in acquiring a golden, and the latter a violet tinge.

2. The preceding blue lost a part of its beauty in acquiring a greenish tinge by its juxtaposition with violet.

3. The above-named violet and a dark indigo blue reciprocally injured each other, the violet, by losing too much blue, resembled violet faded by the light, whilst the indigo blue, in losing its red, acquired an unpleasant greenish tinge.

Assortment of Non-complementary Colours, either in the Combinations of one Simple and one Mixed Colour, or of two Mixed Colours.

143. On placing in juxtaposition colours that have a certain analogy, as a simple red with a mixed red bordering on orange or violet; a simple blue with a mixed blue bordering on violet or green, &c., or two mixed colours, as an orange red with an amaranth red, a greenish blue with a violet blue, &c., &c.; we may observe in the first place, that the two colours will increase in beauty; in the second, that one only will increase in beauty; in the third, that both colours will lose a portion of their beauty. These three cases may be observed in the arrangement of simple non-complementary colours, exhibiting, however, this difference, that the two latter cases will present themselves more frequently than in the arrangement of simple non-complementary colours.

Examples.

First Example.

144. On placing two roses in juxtaposition, one of which is of a certain graduated tone of amaranth red, and the other of a graduated tone of scarlet, and which, when seen separately, are agreeable to the eye, the first will, according to the law, appear more amaranth or rather more blue, and the latter more yellow, which amounts to the same thing as if we were to say, that both lost a portion of red. If these two roses are both at the point where the addition of more blue or more yellow would detract from their beauty, it is very evident that a juxtaposition is injurious to both. If, however, they are beyond the limits of which I speak, juxtaposition will not injure their effect, although it augments the difference between them, provided always that this is not carried beyond the limits named. In fine, if a rose incline too much to yellow, or too much to blue to be seen to advantage separately, it will increase in beauty by being brought into juxtaposition with another rose that is more yellow or more purple.

Second Example.

145. A yellow green in juxtaposition with a green bordering on blue, will lose blue, and will consequently appear more yellow. There are certain yellow greens on which the contiguity of another green would act favourably, and others again on which it would have a bad effect. The first-named would appear more beautiful on being brought near the yellow green of young leaves, whilst the latter would acquire the yellowish rusty green seen in certain leaves as they drop from the trees in autumn.

Third Example.

146. A nasturtium, whose colour is so bright, produces a disagreeable effect when combined with certain purple poppies, the colour of which when seen apart is by no means deficient in beauty. The nasturtium loses its brilliant red, and acquires a dull orange tinge, whilst the poppy assumes an equally dull tinge resembling wine lees.

147. We see from these examples:

1. That in proportion to the analogy of the colours, there is a greater probability that their mutual juxtaposition will be injurious to the effect of one, if not of both.

2. That, if the law cannot, with a view of pleasing the eye, prescribe arrangement of non-complementary colours in as positive a manner as may be done with reference to the assortment of complementary colours, it arises from the impossibility in the present day, of designating with any degree of precision, the innumerable colours of bodies susceptible of being classed under such arrangements, in consequence of our inability to refer them to invariable types, as for instance, Newton's coloured rings. This is the reason that in treating of the distribution of flowers in gardens (118), I have only recommended an assortment of flowers whose colours are complementary, at the same time, that I admit the existence of many other assortments, productive of a very agreeable effect. We see further, from the same examples, that in making ourselves masters of the law, and considering well the effect that we may be desirous of producing in placing two colours beside each other, we shall not be guilty of any fault, I do not say with respect to the harmony of these colours, but with reference to the best possible disposition of which they are susceptible, for the regulation and even augmentation of their splendour, purity, and freshness, as well as for the correction of their individual deficiencies. For the rest, in order to dissipate all further obscurity, I will cite the following examples.

First Example.

148. In the case of a nasturtium, which has such a proportion of red and yellow, that a little more red or more yellow would impair the beauty of the flower, the law indicates, 1. That the vicinity of blue, whose complementary is orange, would produce a good effect owing to the blending of the orange, which has the greatest analogy with the first-named colour; some persons object, however, to this assortment as too harsh:—2. That the vicinity of yellow or red would be injurious to the effect, since their complementaries would cause the

red or yellow of the flower to predominate too much:—3. That if one is obliged to surround nasturtiums with yellow, red, or even orange, these colours must be so deadened as to heighten the brilliancy of the nasturtium from the contrast of the difference in the height of the tone. This latter device of increasing the brilliancy of colours has been known and practised in all times, but I believe no attempt at an explanation of the effect produced was made before the establishment of the law of simultaneous contrast.

Second Example.

149. In the case of a blue agreeably tinged with violet, we must have recourse to green or to grey, whether it border on yellow or green, if we have no orange, yellow, or white to put in juxtaposition with the blue; the contiguity of violet must be avoided, as destructive of that violet tinge of colour which ought to be carefully preserved.

Third Example.

150. In the case of a green unpleasantly tinged with yellow, we must approximate yellow or a rusty yellowish grey.

Fourth Example.

151. In the case of a dull greenish blue, the unpleasant effect of the colour will be neutralized by the juxtaposition of green.

152. If these applications were considered in the art of manufacturing the Gobelin tapestry, there could be no doubt that a knowledge of the law of simultaneous contrast would prevent much error and stumbling on the part of all, who made it their guide in the assortment of coloured threads for copying a given pattern in tapestry, and we ought, therefore, in future to regard this law as one of the most valuable principles of this art.

153. The knowledge of this law is not less indispensably necessary when a comparison has to be drawn, with respect to the beauty of colour, between the dyed woollen and silk threads of carpets, tapestries, or shawls, whose designs are not identical, and whose colours are not uniformly shaded and fused

into one another. In future, therefore, instead of asserting, that the colours of oriental stuffs are superior to our own with respect to brilliancy, the prescribed precautions ought to be taken, in order to avoid all chance of illusion.

154. In speaking of these applications, with respect to the painting of pictures, I think I have said enough to show that painters, who are desirous of regulating their employment of colours according to the law of simultaneous contrast, ought to perfect themselves in *colouring*, just as in linear perspective they study the principles of optics that refer to this department of the art.

155. Patterns exercise so great an influence on the effect produced in tapestry and carpets, that I have deemed it incumbent upon me, owing to the numerous observations I have had occasion to make in the Royal manufactories, to offer some reflections on the kind of painting most suitable for this purpose. These remarks may interest artists who occupy themselves with works of this nature, and who endeavour to comprehend the principal object of this species of imitation. After having determined what are the principal effects which they ought to attempt to produce, they will see what points of ordinary painting can be sacrificed to attain to the former; and they will thus be able to draw a conclusion as to what has to be done for the perfection of the special part of their copy. They will doubtlessly perceive, that patterns of flowers for furniture do not require to be painted in the manner that a pupil of V. Spaendonk would make a drawing for a work on botany; that patterns of figures intended for tapestry must not resemble miniatures in finish, and, finally, that in all these productions, *the objects ought to be as large as possible, and present absolutely fine effects of colour.*

156. I have established this proposition upon the nature of the coloured elements employed by the manufacturer, (of tapestry, carpets, &c.,) and upon the distance at which these works ought to be viewed. If I am not mistaken, reasons analogous to those I have employed to prove this proposition, may present the means of establishing, in an ostensible manner, the true principles of several of the imitative arts, and these principles being once deduced from the specialty of the art to which they

refer, afford the means of distinguishing between the efforts by which we may hope to arrive at true improvements, and such as can only tend to a contrary result.

157. I have endeavoured to show, that some of the imitative arts have a more intimate connexion with paintings done in plain tinting than with those of the chiaro-obscuro style, basing my propositions on the following facts:—

1. The eye experiences incontestible pleasure in seeing different colours, and for this reason, the wainscoting of the most elegant apartments is generally painted in various colours.

2. This pleasure, which may be compared to the enjoyment of taste, is augmented when bright colours are disposed in such a manner, as to recall to mind an agreeable object, even if it be not perfectly represented.

From this I have concluded, that when we wish to affect the eye by colours under the following circumstances:—

1. When these colours are seen at such a distance, that the finish of an elaborate painting would be lost, and,

2. When a painting is nothing more than an accessory employed in the decoration of an object, the use of which is at variance with the employment of any more elaborate workmanship, which would besides be of too expensive a nature;

copies ought to be made in plain tinting rather than according to the contrary method of painting; and choice should be made of such objects as are most remarkable from their beauty of colour and simplicity of form, as flowers, insects, birds, &c.

In the course of lectures which I gave at Lyons in 1842 and 1843, I entered into an exposition of the contrast of colours as applied to the manufacture of silk stuffs. It was with this object in view that the Society of Agriculture and Useful Arts, in the first place, and the Chamber of Commerce at Lyons subsequently, petitioned the Minister of Commerce that I might repeat the same course of lectures in that city, that I have delivered every two years in Paris since 1828. It was, therefore, in the wish of complying as far as I was

able, with the intention of the industrial bodies at Lyons, that, prior to the commencement of my lectures in that city, I devoted myself to the researches which I deemed necessary to prepare me for the instruction of the designer and the manufacturer, whose mutual co-operation is indispensable to the perfection of stuffs presenting the best possible assortment of colours, both as to their mixture and their mutual opposition. These researches, which were made subsequently to the publication of my work on Simultaneous Contrast of Colours, in 1839, will compose the materials for the work I purpose to bring out under the title of *Théorie des Effets Optiques que presentaient les Etoffes de Soie;* and of which I am going to present a very concise extract to the Academy.

In my endeavours to reduce the optical effects of silk stuffs to a theory, I soon perceived the necessity of placing them relatively to the spectator under the most perfectly defined, and the smallest number of conditions. There are four principal conditions in which the same stuff may be seen by a spectator standing with his face turned to the light, or, on the contrary, with his back against the light. The importance of distinguishing between these four conditions will be understood when I have spoken of the effects of light reflected by a system of contiguous parallel metallic cylinders.

First position of the Cylinders.—They are laid on a horizontal plane, and their axis is in the plane of incident light.

First condition.—The spectator, standing with his face to the light, sees the cylinders very strongly illumined, owing to his receiving much light irregularly reflected.

Second condition.—The spectator, turning his back to the light, sees the cylinders darkened, since he receives but little light, and that irregularly reflected.

Second position of the Cylinders.—Their axis is perpendicular to the plane of the incident light.

Third condition.—The spectator, having his face turned to the light, sees the cylinders less strongly illumined than in the first condition, since the only light that reaches him is reflected by a narrow zone from the highest part of each cylinder.

Fourth condition.—The spectator, turning his back to the light, sees the cylinders very strongly illumined, owing to

each one being accompanied by a broad zone reflecting light as by a mirror.

The cylinders when seen in the first and second position, when the spectator faced the light, appeared to be unequally illumined; but the difference in the quantity of the light transmitted by them in the first and third conditions is much less than will be the case on observing the cylinders when the back of the spectator is turned towards the light, and for this reason, that, in the second condition, they present the *maximum of shade*, and in the fourth the *maximum of light*.

The effects of which I have been speaking may be observed with cylinders of ·6, ·04, and ·02 of an inch in diameter. By the aid of two systems of metallic cylinders, which I place upon the table, we are able to demonstrate that the optical effects of the smaller cylinders are more strikingly marked than those of larger diameter. I must add, that threads of smooth silk, when arranged parallel to one another, have the same effect as systems of metallic cylinders, and, on that account I purpose speaking of the optical effects of metallic cylinders before I treat of those exhibited by silk stuffs. It remains for me to prove by experiment the truth of my assertion.

All woven stuffs are composed of two systems of parallel threads, forming the warp and the woof; and are arranged perpendicularly towards each other.

Silk stuffs are plain (A), or not figured, and (B) figured.

A. *Plain or Unfigured Silks.*

Plain silks are comprised under two heads: the first, showing only on the right side one system of threads, constituting either the warp or the woof; the stuffs of the second kind show both the warp and the woof.

Plain Stuffs of the First Division.

First Section.—Stuffs whose effects correspond to those of a system of parallel cylinders.

I am about to show the identity of the optical effects of contiguous and parallel metallic cylinders, with those of satin and cut or terry velvet.

Satin.

Satin is a stuff, the warp of which is alone seen on the right side, in the form of small parallel cylinders, whose extremities disappear in the interior of the stuff itself by the action of sizing and dressing, which is indispensably necessary to secure the threads in the places in which it is intended they are to remain. The joinings of the sizing are irregularly distributed, in order that, by concealing them as much as possible, the surface of the satin may appear alike smooth and shining.

Satin is ordinarily made with the warp, but it may also be made with the woof.

Cut Velvet.—Velvet termed Epinglé, or Terry Velvet.

This is a fabric having transversely formed hollow flutings or ribs which are produced by means of a cylindrical bar of iron, which, after having been covered by the warp, is separated from it in such a manner that the rib remains hollow throughout its whole length, presenting on the exterior the appearance of a cylindrical surface formed by the warp.

In order that the optical effects presented to the spectator should be what we have described, every rib formed by the warp ought to exhibit the latter as nearly as possible in the form of equal rings, parallel to one another, and perpendicular to the axis of the cylinder which they represent.

Now, suppose we place two cuttings, *a* and *b*, of the same satin upon any horizontal plane, in such a manner that the threads of the warp or the woof of the satin, according as the case may be, of the piece *a* shall be perpendicular to the threads of the piece *b*, the effect will be identical with that produced by metallic cylinders, when observed under the same circumstances.

The same results were obtained on making the experiment with cut velvet, but less difference was observed between the two pieces of velvet than had been noticed in the case of the satin, owing to the surface of the cylinders for the velvet being transversely ribbed instead of smooth, in consequence of these cylinders being formed by threads wound perpendicularly round

the cylindrical peg or shuttle, whose form they reproduce in this manner.

In order that we may duly appreciate the influence that flutings or transverse channelings may have on the effects of light, we will now consider the manner in which light is reflected in a system of transverse flutings.

Reflections of Light from transversely fluted Cylinders.

I place upon the table metallic cylinders having transverse flutings of various depths, by means of which the following facts may be demonstrated.

First position of the Cylinders.—They are laid on a horizontal plane, and their axis is on the plane of incident light.

First condition.—The spectator, standing with his face to the light, sees less light reflected than from the smooth cylinders, owing to the flutings diminishing the extent of the surface, which, in the smooth cylinders, reflected light as from a mirror.

Second condition.—The spectator, turning his back to the light, receives a very strong reflection of light, as his eyes are directed towards the face of each fluting, on which the light falls.

This result is inversely the same as that observed in the plain cylinders.

Second position of the Cylinders.—Their axis is perpendicular to the plane of incident light.

Third condition.—The spectator, when facing the light, sees the cylinders brighter than they were in the first condition: the result is, therefore, inversely the same as that obtained with the plain cylinders.

Fourth condition.—The spectator, when standing with his back to the light, sees the cylinders less brilliant than in the second condition, and much less so than in the plain cylinders.

We may, consequently, define the results of the reflection of light by transversely fluted cylinders as the reverse of those produced by smooth or plain cylinders.

Second section.—Stuffs, whose effects correspond to those of a system of cylinders fluted perpendicularly to their axis, and parallel with one another.

While we are ignorant of the manner in which light is reflected by cylinders, with smooth or transversely fluted surfaces, we must be at a loss to explain how cut velvet, with its projecting ribs, will appear in the light, when compared with satins whose surface is so uniformly smooth. Our astonishment is still more increased when we observe *reps* (ribbed silks,) which, like cut velvet, have marked ribs, acting upon light differently from the latter tissues. After having compared together the reflection of light on the surface of smooth cylinders and on that of transversely fluted cylinders, we shall be able by the aid of the lens to discover the analogy existing between the surface of ribbed and fluted stuffs, *bazinettes**, and *dimities*†, with that of transversely fluted cylinders, and our surprise will then cease as we find an explanatory cause for effects which had struck us as so strange.

Reps, (ribbed silk properly so called,) or *reps par le trame*, (ribbed in the woof,) presents an appearance of ribs, the warp of which forms the axis; the intermediate space between the threads of the warp forming the rib, gives rise to longitudinal furrows. The woof entirely covers the warp on the right side, in the form of cylindrical or flattened rings, each of which is separated from the next by transverse furrows, generally more strongly marked than the transverse furrows of the cylindrical ribs of cut velvets.

I lay upon the table some specimens of *reps par la trame*, (silks ribbed in the woof,) presenting precisely inverse phenomena from those of satins and cut velvets.

It is certainly very remarkable, that these last-named stuffs with their ribs should produce the same effect as satin, the surface of which is the smoothest presented by any stuff, whilst they exhibit the inverse effects to those of reps, (ribbed stuffs,) to which they approximate so closely by their ribs.

Reps par la chaîne, (stuffs ribbed in the warp,) *bazinettes*, (which only differ from stuffs ribbed in the woof by the inequality in the width of the different ribs,) and *dimities*, (differing

* *Bazinette*, a muslin made of silk and wool, the ribs of unequal width.—*Tr.*

† *Dimité*, a muslin made of silk and cotton, (the ribs very wide but equal.) Both are varieties of what in the trade in this country is known as *Mousseline de soie.*—*Tr.*

in the size of the ribs,) produce the same effect upon light as stuffs ribbed in the warp, and consequently as cylinders having transverse flutings.

Third section.—Mock velvet, or velvets with cotton backs. There are certain stuffs termed mock velvet, which resemble cut velvet, and like the latter have transverse ribs; instead, however, of their being hollow, they are filled up by a cotton or silk woof, in order to prevent the effect so easily produced on the hollow ribs of cut velvet by external pressure or friction. Mock velvets have a closer analogy with ribbed stuffs than with cut velvet, when we consider the optical effects they produce, especially if we look at them with our face turned from the light as in the second and third conditions; but if the spectator face the light, he will be able to observe specimens of this stuff, which are more illumined in the first than in the third condition, and they will then produce the same effect as cut velvets.

Conclusion.—All plain stuffs which exhibit on the right side only one system of the thread constituting them, act upon light in a similar manner: as,

1. A system of smooth contiguous and parallel metallic cylinders: for instance; satins, whether showing the warp or the woof; cut velvet, called terry velvet.

2. A system of fluted transverse and parallel metallic cylinders. Reps, showing the warp or the woof; bazinettes, *composed of silk and wool;* dimities, *equally striped, silk and cotton.*

3. The greater part of mock velvet stuffs act upon light in the same manner as reps, but there are some which present to a spectator, having his face turned to the light, effects analogous to those of terry or cut velvet.

Plain stuffs of the second division.—The stuffs that simultaneously show both the warp and the woof are very numerous; such for instance are gauze, crape lisse, taffetas, including Florence silk, sarsenet, and taffetta properly so called, louisines, gros de Naples, pou de soies, satin turque; various serges, comprising Levantine, Virginie, and Filoché*.

* *Serge* is a coarse black twilled silk, and Levantine, Virginie and Filoché mere varieties of the same, known to silk-merchants in this country by the same names.—*Tr.*

The surface of these stuffs may either be plain or both striped and *granular**. In all these cases, the optical effects produced by the reflection of light are referrible to the preceding principles. These stuffs, therefore, when seen by a spectator standing with his face to the light, exhibit both the warp and the woof, and the effects produced vary with the position of the warp relatively to the plane of the light, and according to the predominance, subordination, or equality of the warp with reference to the woof.

In order properly to appreciate the influence of each of the elements of which I have spoken, with respect to the optical effect of a pattern of a plain smooth stuff belonging to the second division, we must first consider *glacé*, or shot stuffs†, that is to say, stuffs which have the warp of one colour, *z*, and the woof of a colour, *y*, or the warp of one colour, *z*, and the woof composed of two threads, one of which is of the colour *y*, and the other of a colour *x;* and in order further to take into account all the optical effects that may be observed, we ought to have recourse *to the principle of a mixture of colours*, and to the principle of regulating their contrast.

Conformably to the first of these principles, red mixed with yellow gives orange; yellow mixed with blue, green; red mixed with blue, violet; and, finally, red mixed with green, yellow mixed with violet, blue mixed with orange, produce black or normal grey.

Further, conformably to the principle of simultaneous contrast of colours, when there are two parts of the surface of the same stuff placed side by side, but so as to present two unequally illumined, or differently coloured surfaces, these surfaces will appear as dissimilar as possible, with respect to brightness and colour, if one only or both are coloured; and in this case the modification is effected by the addition of the complementary colour of one of the surfaces added to that of the other surface. The following are the four principles to which those effects are definitely referrible, which it has been the object of the present work to explain.

* The name of the kind of silk answering to *grenue* is *grenadine.—Tr.*

† Silks *shot* with one colour are termed *glacé*, or properly speaking, shot, and *chameleon* when shot with several colours.—*Tr.*

1. The principle of the reflection of light, by a system of contiguous and parallel metallic cylinders.

2. The principle of the reflection of light, by a system of metallic cylinders fluted perpendicularly to the axis.

3. The principle of the mixture of colours.

4. The principle of the simultaneous contrast of colours.

I will present some examples of the optical effects of glacé or shot stuffs.

First Example.—A piece of *gros de Naples*, the warp of which is blue and the woof red, will appear violet to a person turning his face towards the light; if the warp be in the plane of light, the violet will be redder than in the opposite case; this is in conformity with the principles of the reflection of light by metallic cylinders, and with the principle of the mixture of colours.

The same stuff seen by a person turned from the light, appears red if the blue warp be on the plane of incident light, and blue if the warp be perpendicular to this plane, and this in conformity with the principles of reflection by a system of metallic cylinders.

Second Example.—A stuff which has a blue warp, and a woof formed of two threads, one of which is yellow and the other red, will appear of a slightly coloured grey to a person facing the light, in consequence of the three colours not being exactly neutralized. These effects are produced conformably to the principles of the reflection of light by cylinders, and to the principle of the mixture of colours.

The same stuff seen by a person with his back turned from the light appears, 1. *blue*, if the plane of the light be perpendicular to a blue warp; 2. *yellow*, if the warp be on the plane of light, and if it be the yellow thread that is presented to the eyes of the spectator; 3. *red*, if the warp be in the plane of light, and if the red thread of the woof present itself.

Such is the simple explanation of the effects exhibited by the shot silk stuffs known as *chameleon* silks.

I should exceed the limits of this extract, were I to take other examples of the glacé or shot stuffs suited to the application of the principle of the contrast of colours. I will, therefore, present only three patterns of stuffs not shot, formed:

(*a*) 1. One uniformly white stripe, and another likewise white, but open figured stripe; the latter will appear grey;

(*b*) 2. One uniformly thick yellow stripe and a white open-worked stripe; the latter will appear lilac, from the effect of the complementary to the yellow of the thick stripe;

(*c*) 3. One uniformly thick violet stripe and an open-worked white stripe; the latter will appear of a straw colour, owing to the effect of the complementary to the violet in the thick stripe.

By an application of the researches I have made I have been able to solve the following question: in manufacturing a gros de Naples that is to be shot with two given colours, which of the two should constitute the warp? my answer is, *the darker, or the least bright.*

Examples.—Blue and orange shots, or blue and yellow, violet and orange, and violet and yellow, are very beautiful when the warp is blue or violet, but when the opposite is the case, the effect is bad.

When a shot silk is to be made with one colour and white, the colour must be used in the woof, and the white consequently in the warp; the result is not contrary to the first named, as I have demonstrated in my work.

Watered Stuffs.

The term watering, *moire*, is applied to designs produced by means of pressure suitably applied to ribbed stuffs.

In order that the watering may produce its proper effect, it is necessary that the ribs of the stuff should have a certain saliency, and this can be effected by the pressure to which the stuff is subjected being applied unequally to the different parts of the same rib, and obliquely to its axis, as I am about to show.

Watering presents different patterns, according as the stuff is pressed, after having been folded in two longitudinally, or after being placed in several transverse folds, or, finally, after pressing two perfectly similar pieces with their right sides in contact; modifications in the watering are likewise produced

by drawing and stretching the stuff, or running the dye perpendicularly to the axes of the ribs towards symmetrically arranged points, by which means undulating lines are formed in the direction of this originally rectilinear axis.

Theory.—If the sides of the two right side surfaces in contact were laid exactly the one over the other, and if one piece of stuff were folded together, either in a transverse or longitudinal direction, or if we had two like stuffs applied, the one against the other, there would be no *water* if the perfectly homogeneous sides did not mutually produce and receive impressions *perpendicular* to the axes of the ribs, which I suppose to be included in the same plane, and symmetrically arranged relatively to the rings of the ribs produced by the warp; this is the case with gros de Naples, which is a stuff peculiarly fitted to receive the impression of watering; if these conditions be not fulfilled there will be a mere smoothing or crushing of the salient parts, and the stuff will consequently resemble smooth-faced tissues. As, however, this homogeneous condition of the ribs, and pressure perpendicularly applied to their axes, cannot be practically effected, one rib in coming in contact with another or a different portion of its own extent exercises, at different points of its length, an unequal pressure obliquely to its axis, at the same time that it experiences a similar pressure from the rib opposite to it; consequently, the initial symmetry of the different parts of each rib is deranged.

Before examining the optical effects of the whole of the ribs constituting a watered stuff, I will describe the modifications undergone by a single rib in its whole extent, by the process of watering.

The essential modification experienced by one of the ribs in this process, is, that instead, as before it was watered, of exhibiting on the right side a perfectly identical cylindrical surface, having fine transverse furrows, it assumes a prismatic form, appearing different at different points, and at different points of view, the rib being undulated instead of rectilinear.

Thus, when on facing the light we look only at one side of a stuff having its ribs perpendicular to the plane of light, and being placed on a horizontal plane, there is one part that will appear under the form of a dihedric angle, one of whose sides

may be completely light and the other dark; another portion of this rib will present one side on an inclined or horizontal plane, which affords an excellent means of observing the effect of the pressure on the whole of the threads, perpendicular to the ribs, which, before the tissue was watered, constituted the rings. In fact, the latter present a series of small shining and satiny elliptical figures occasioned by the flattening to which they have been subjected; these two portions come in contact with a third, which appears, from the manner in which it reflects light, to have been twisted, as it were, but which, in consequence of the compression applied obliquely to its axis by a rounded rib, resembles a furrow, one extremity of which seems turned forward and the other backward. We may observe by the lens that the small and silky ellipses of the furrow are folded together in the direction of their smaller diameter.

On ravelling out the threads of a coarse watered stuff, and taking those on the interior of the rib, we may observe how the whole of the threads are compressed, appearing prismatic and twisted as it were, and being, besides, furrowed perpendicularly to their length from the effect of the pressure of the rings which partially cover them on the right as well as the wrong side.

As the different ribs of a stuff that is not watered are all parallel to, and dependent upon one another like parts of the same system of a tissue, there will always be contiguous parts belonging to different ribs which will necessarily experience similar modifications, and in the same direction, from a like action; and when we add to this, the effect of drawing or running the dye towards points symmetrically placed along the length of one rib, and which may be applied perpendicularly to the axis of this rib, it will be easily understood that contiguous and mutually dependent parts, experiencing the same modification, will present an appearance of zones of a certain width and a certain symmetry.

On examining with the lens a watered stuff, laid upon a table, in such a manner that the ribs are perpendicular to the plane of incident light, these effects will be made apparent; when all the strongly shaded parts appear like the posterior

faces of a certain number of dihedric angles of the contiguous ribs, the parts in half shade will look like parts of the anterior and posterior faces of dihedric angles made visible by the inclination these portions of the ribs have received by the pressure to which they have been submitted; and, finally, it will be observed that the luminous parts belong to portions of the ribs, which, having been strongly compressed, exhibit the horizontal or slightly inclined face of a flattened prism.

On looking at the wrong side of a watered stuff the watering is perfectly apparent, although there is not the same inequality in the saliency of the different parts as on the right side; we may likewise perfectly well distinguish the undulation by the action of watering on the axis of the rib, which was originally rectilinear. We will distinguish two kinds of watered stuffs: the first comprising *monochromatic watered stuffs*, and the second, *watered stuffs;* as the process of watering is alike applicable to monochromatic and to shot stuffs. The question here arises: is the process alike advantageous to both kinds? This subject has been treated in detail in my work, and the researches to which its consideration have given rise have led me to the conclusions I am about to give in a very concise form.

There is this great difference between a monochromatic watered stuff, and a shot stuff not watered, that the former appears to the greatest advantage when presenting to the eye broad plane surfaces covered with designs of great simplicity, possessing a certain mobility and a variety of aspect which does not injure the effect, whilst a shot material, not watered, must be laid in folds, as when made into articles of wearing apparel, before it will present the effects which make it so much admired, and which exhibit a variability of colours according to the position in which the spectator observes them, and which thus acquire the *apparent mobility* of watered stuffs, without, however, assuming the form of the undulating figures that are characteristic of the last-named tissues. If, on the contrary, folds are not injurious to the effect produced by a watered stuff, it must be admitted, that it appears to the greatest advantage when seen smoothly stretched, as in articles of upholstery, or even as the cover of a book in the most elegant forms of binding.

We thus see that the most special use of watered and shot stuffs is entirely in accordance with the preceding considerations; add to this, that patterns of watering do not cut the colour of the stuff more than by the opposition of shade to the light, whilst the effect of a shot may present the most extreme opposition of colours without losing their beauty.

The possibility of combining in one stuff the effects of watering with those produced in a shot stuff, depends upon the essential difference existing between these effects, and we cannot therefore assert *à priori*, that the combination will, of necessity, give rise to confusion.

I will now give an exposition of the facts demonstrated by experiment regarding this question.

Monochromatic Watered Stuffs.

The beauty of a watered stuff is based upon a taste for the design, and pleasure in the appearance of a simple form, presenting an apparent mobility and variability, which in no way detract from the good effect of the whole, and, consequently, to attain to the maximum of the effect of which this stuff is susceptible, it ought to present as simple an image as possible, in order to exhibit a light, mobile, and, as it were, airy appearance. This is the effect produced by watering in the greater part, if not in all, monochromatic stuffs.

Shot-watered Stuffs.

The beauty of a shot stuff, consisting in the contrast of its colours, its metallic brilliancy, and the lightness of its shades, which call to mind the most varied tints of clouds lighted by the sun, place it in the greatest possible opposition to the beauty of the effects produced in watered stuffs. Besides this, a shot-watered stuff, presenting as it does a great contrast of colours amongst the different parts of the design, loses much of the beauty it would possess if it were monochromatic.

I conclude incontestibly from this fact, that every shot stuff, in which the colour of the warp and that of the woof are employed in the most suitable manner, loses by the process of watering.

All shot stuffs do not, however, lose alike by the process of

watering, and as in the opinion of some persons, watering may add to the good effect of shot stuffs, I will speak of those cases in which, if it be not decidedly advantageous, it is not at any rate injurious.

The disadvantageous effect produced by watering will be in proportion to the degree of opposition between the colours of the warp and the woof; for instance, blue and violet, and blue and green, produce shots, the watering of which is sufficiently homogeneous to excite the admiration of many.

Finally, watering is decidedly advantageous to a shot stuff rendered defective by any inequality in the threads, either by lines or bars, since the process of watering destroys the effect, by interrupting more or less the continuity of the lines.

B.—Figured Stuffs.

The last part of my work is devoted to the consideration of *figured stuffs.* Before I speak of their effects, I will examine the six general cases, which they present relatively to the disposition of the threads, and the influence thus exercised on the optical effects produced, putting the subject of colour entirely out of the question.

First case.—*A figured stuff presenting but one sole effect, either of the warp or the woof.*

Second case.—*A figured stuff, presenting simultaneously an effect of the warp and the woof.*

Third case.—*A stuff, presenting an effect produced by the warp upon a ground of taffetta silk.*

Fourth case.—*A stuff, presenting an effect of the warp upon a ground of a kind of taffetta silk.*

Fifth case.—*A stuff, presenting the effects produced, both by the warp and by the woof, upon a ground of a kind of taffetta.*

Sixth case.—*A stuff, presenting effects arising from a web of taffetta on a ground of the same kind of web.*

To this part of my work appertains especially the application of the principle of the contrast of light, since two or more colours may be employed in forming not only a shot, but definite and permanent figures.

The following table indicates the arrangement of the subjects composing the work, of which I have given the shortest

possible extract. In completing my work at a distance from Lyons, I should have experienced great difficulties in speaking clearly of many circumstances connected with the weaving and manufacture of silken stuffs, if I had not had recourse to the aid of M. Piobert, our excellent brother Academician, whose profound knowledge on these subjects and whose obliging assistance have contributed to render this work less imperfect than it would otherwise have been, and I most gladly avail myself of this opportunity to express my obligation to him.

TABLE.

First Point of View.—Smooth plain monochromatic stuffs considered relatively to the effect which the warp and the woof may have upon the reflection of light.

First Division.—Monochromatic stuffs, the essential optical effects of which may be exclusively referred to the warp or the woof.

First Section.—Monochromatic stuffs with a smooth surface, and monochromatic stuffs with a ribbed surface, the optical effects of which correspond with those of a system of parallel cylinders.

1. Stuffs with a plain or smooth surface, as satins, showing the warp or the woof.
2. Stuffs with a ribbed surface, as cut velvet, called terry velvet.

Second Section.—Monochromatic stuffs with parallel ribs, the optical effects of which correspond with those of a system of parallel cylinders fluted perpendicularly to their axes.

1 and 2. *Reps* ribbed in the woof, or in the warp and fluted.
3. Bazinettes (silk), muslin made of silk and wool.
4. Dimities (silk), muslin made of silk and cotton.

Third Section.—Monochromatic stuffs having parallel ribs, the optical effects of which correspond both with those of a system of parallel cylinders, and with those of a system of cylinders fluted perpendicularly to their axes.

Certain Mock or Imitation Velvets.

Fourth Section.—Monochromatic stuffs having parallel ribs, the optical effects of which correspond with those of a system of parallel cylinders, fluted in such a manner as to appear equally light in the first and third conditions.

Certain Mock or Imitation Velvets.

Second Division.—Monochromatic stuffs, whose optical effects are referrible both to the warp and the woof.

First Section.—
- Gauze.
- Crape lisse.
- Florence silk.
- Sarsenet.
- Taffetta.
- Louisine.
- Gros de Naples.
- Pou de soie.
- Satin turque. (Also Turquoise, so called from the colour.)

Second Section.—
- *Sergé*—Coarse black twilled silk.
- Virginie

Third Section.— Filoché } varieties of the same.

Second Point of View.—Smooth plain stuffs, the warp and woof of which are apparent, and exhibit two different colours.

Shot Stuffs.

First Section.—Shot stuffs having a monochromatic woof.
Second Section.—Shot stuffs having a bichromatic woof.

Third Point of View.—Plain monochromatic stuffs, or shot stuffs considered relatively to the process of watering.

Watered Stuffs.

First Division.—Watered stuffs.
Second Division.—Shot watered stuffs.
First Section.—Shot watered stuffs having a monochromatic woof.
Second Section.—Shot watered stuffs having a bichromatic woof.

Fourth Point of View.—Stuffs considered with reference to *fixed* patterns, that is to say, such as preserve their tints whatever be the position in which they are considered.

Figured Stuffs.

First Division.—Monochromatic figured stuffs, the optical effects of which are exclusively referrible to the warp or to the woof.
Second Division.—Monochromatic figured stuffs, whose optical effects are simultaneously referrible to the warp and the woof.
Third Division.—Figured stuffs, whose optical effects are referrible to the different tones of the same colour exhibited in the threads.
Fourth Division.—Figured stuffs, whose optical effects are referrible either to the threads of one colour, or of several colours being combined with white, black, or grey threads, or to threads of many colours combined together, including white, grey, and black.

The work, of which the above is a short extract, was published in the last session of 1846, at the expense of the Chamber of Commerce at Lyons.

VI.

MEMOIR.

ON THE LATENT HEAT OF STEAM AT DIFFERENT PRESSURES.

By V. Regnault.

My object in the present memoir is to determine the amount of heat necessary to convert 1 kilogramme of water at 0° into steam at different pressures. I shall express these quantities of heat by designating the number of kilogrammes of liquid water they are able to heat from 0° to 1° centigrade.

In the middle of the last century, Black was the first who made the important observation that, a large quantity of heat was absorbed in the formation of steam, or instituted experiments for the purpose of measuring this quantity. His manner of proceeding was as follows. He placed a small vessel full of water on the top of a cast-iron stove, in which a fire was kept up with sufficient regularity to admit the assumption, that the vessel received in equal periods of time pretty nearly equal quantities of heat; and he then made comparisons between the time it required for the water to come to the boiling-point, and the time required for the same water completely to boil off. This experiment, although sufficient to demonstrate the absorption of heat which takes place during evaporation, is too rough to give the result in strictly accurate measurements. Black

was himself aware of this fact, and he subsequently in concert with Dr. Irvine, instituted new experiments, in which he made use of the method of mixtures, which he had devised for the purpose of determining the specific heat of bodies. He made use to this effect of an ordinary still, and measured the elevation of temperature experienced by the cold water surrounding the worm, by the condensation of a certain quantity of steam. Black thus obtained 530 degrees Cent., which is much too low, owing to his not having taken into account the necessary corrections*.

The celebrated Watt made experiments on this subject at various intervals, and was first led to direct his attention to the subject at the suggestion of Black, whose pupil he had been. Watt's first observations date from 1765, and yielded him the number 766, which, however, he himself regarded as inaccurate. He resumed the subject in 1781, and then made the experiments, described by himself in the article *Steam* in Robison's *Mechanical Philosophy.* (Brewster's Edition, vol. ii., p. 5.) The mean of 11 determinations gave the number 625·2, but this was regarded by Watt as too low, and he adopted as a more probable number, 633·3.

Rumford attempted to determine the same element by means of his calorimeter. Water was put in a glass retort, the neck of which rising up was inserted by a cork in the mouth of the worm of his calorimeter.

Rumford† thus found the numbers 669·0, 670·8, and 671·9 in three different experiments. These numbers are too high. In the method pursued by Rumford, a certain quantity of steam was condensed in that part of the neck of the retort within the calorimeter, which imparted heat to it, although it fell back into the retort in a liquid state.

Dr. Ure published a memoir in the *Phil. Trans.* 1818, p. 385, in which he proposed to determine the latent heat of evaporation of a certain number of volatile substances. Ure's experiments were made with a simple apparatus, which, however, was ill adapted for yielding precise results. It consisted of a small glass retort, having a short neck which entered into a

* *Lectures on the Elements of Chemistry*, vol. i.

† Biot, *Traité de Physique*, t. iv., p. 710.

receiver of thin glass, of a spherical form, and 3 inches in diameter. This receiver was surrounded by a certain quantity of water enclosed in a glass cylindrical vessel. 200 grains of the liquid to be tested was put in the small retort, and rapidly distilled by means of an Argand lamp. The water of the small calorimeter was continually agitated by means of a thermometer, which indicated its temperature. Dr. Ure by this method found the number 637·5 as the representative of the quantity of heat required to reduce a kilogramme of liquid water at 0° to steam at a pressure of 760 millimeters. It must, however, be observed that the results arrived at by Dr. Ure were calculated with an incorrect formula, as has already been mentioned by M. Brix (*Poggendorff's Annalen*, LV., p. 351), and that the preceding number becomes reduced to 593·4 on applying the true formula to the numerical data of his experiment.

Dr. Ure states in the memoir already cited, that Lavoisier and Laplace had found the number 655, but I have sought in vain for this determination in the memoirs published by these illustrious authors.

We find in the *Traité de Physique*, by Biot, t. iv., p. 713, that Gay Lussac on the one hand, and Clément and Desormes on the other, have obtained the same number, viz. 650; but I have nowhere been able to find the details of their experiments.

The most important and recent experiments made on the subject under consideration are due to Messrs. Despretz and Brix.

In a first series of experiments (*Annales de Chimie et de Physique*, t. xxiv., p. 323) Despretz made use of an apparatus similar to the one employed by Rumford. The mouth of the retort enclosing the liquid entered into a copper worm which passed through an oblong and rectangular box of the same metal, and came out through one of its walls; the condensed liquid passed through the worm and fell into an external vessel so arranged as to receive it. The box held 2703 grammes of water. Despretz found the number 631 for the total heat.

In a second series of experiments, Despretz made use of a calorimeter of much larger dimensions, which was capable of

containing 30 liters of water. The condensed liquid remained at the bottom of the worm and could be weighed with exactness. This series gave a higher number than the former, namely 640.

M. Brix in his memoir (*Poggendorff's Annalen*, LV., p. 341) entered into an elaborate discussion of the different causes of error that may affect the results obtained by the method of mixtures, when used to determine the latent heat of steam, and he endeavoured by a long course of careful investigation to render the sum of the errors as small as possible. M. Brix's principal object was, however, to determine the latent heat of other liquids than water; and it was probably on that account that he made use of an apparatus of such very small dimensions. (Fig. 1, Plate I.)

In this case, the sum of the corrections necessarily acquires a very large relative value, and consequently throws more uncertainty upon the absolute value sought.

However this may be, M. Brix deduced from his experiments on steam, the same number 640, which was obtained by M. Despretz in his second series of experiments.

It may be seen from the preceding remarks that the numbers obtained by different experimentalists differ considerably from one another; but it must be observed that the experiments of Messrs. Despretz and Brix, which merit most attention, lead to the same result. The number 650 has been generally adopted in practical mechanics.

The labours that I have enumerated were solely directed to the determination of latent heat of steam under ordinary atmospheric pressure; while the experiments, whose object it has been to determine the same element under different pressures, are very imperfect, and much less numerous.

Watt admitted that the quantity of heat necessary to convert 1 *kilogramme of water at* 0° *into steam at any pressure, is constant;* consequently, this quantity is always the same whatever be the temperature of the steam, provided the latter is in a state of saturation.

This proposition which is known as *Watt's law* ought rather to be regarded as an hypothesis of this celebrated mechanician, since he did not establish it by direct experiment, but simply

made one experiment under a lower pressure than that of the atmosphere, and this was admitted by Watt himself to have been very imperfect*.

Southern and Creighton made more carefully-conducted experiments in 1803, to determine both the density of steam at different pressures, and its latent heat under the same conditions. Their observations are incorporated in a letter addressed to Watt, and which has been published by Robison, in his *Mechanical Philosophy*, vol. ii., p. 160.

In a first series of experiments, Southern found that the latent heat of steam may be represented by the following numbers:

515·5	at a pressure of	1016	Millimeters.
541·1	„	2032	„
534·0	„	3048	„

In a second series, which he regards as more exact than the former, the same physicist found:

523·3	at a pressure of	1016	Millimeters.
523·3	„	2032	„
527·7	„	3048	„

Southern concludes from these experiments that *the latent heat of evaporation*, that is to say, *the heat absorbed in the transition from the liquid to the gaseous state, is constant at all pressures, and that the total quantity of heat may be obtained by adding to the constant latent heat the number representing the temperature of the steam.*

This law is known to physicists as *Southern's law.* Clément and Desormes made new experiments on this subject in 1819. They made use of a large boiler, in which the water might be brought into ebullition at different pressures, and caused equal quantities of steam to be condensed in a refrigerator containing the same quantity of cold water, taken at the same temperature in each experiment. They thus discovered that the refrigerator acquired the same temperature at the close of every experiment, whatever the pressure might have been at which the steam had been formed. The experiments of Clément and Desormes thus confirmed *Watt's law.*

* See "*Mechanical Philosophy*," by Robison, vol. ii., p. 8.

The labours of these physicists are only known through an extract published by M. Thenard in his *Traité de Chimie*, vol. i., p. 78, and communicated directly to him by one of these observers. This extract will be found in the accompanying note*.

In order to complete the historical sketch of the attempts that have been made to determine directly the question before us, I must not omit to mention that M. Despretz states in his *Traité de Physique*, 4th Edition, p. 212, that he had made some experiments to determine the latent heat of steam at great pressures, but that he had been arrested in his course by the dif-

* The experiments of Clément and Desormes were made in the following manner. They made use of a large boiler, in which the steam might be made to acquire an expansive force of several atmospheres. A copper pipe of a small bore was made to conduct the steam into a trough, containing a mass of cold water, weighing 290 kilogrammes; the escape of the steam being regulated at will by means of a cock. A manometer, placed upon the conducting steam pipe, indicated the degree of tension, whilst a thermometer marked the amount of temperature.

In the first experiment, the steam had a tension of 4 atmospheres, and a temperature of $152°\frac{1}{2}$. $14\frac{1}{2}$ kilogrammes of steam were introduced into the cold water; the time occupied in the process did not exceed two minutes. The temperature of the water was previously 20°, and subsequently $49°\frac{1}{4}$.

The quantity of heat before the experiment is represented by .... 290 kil. at +20° = 5800 units.
After the introduction of the steam, by 304.50 „ at $+49°\frac{1}{4}$ = 14972 „

The $14\frac{1}{2}$ kilog. have thus yielded .... 9772.
and consequently 1 kilog. yielded .... 632.

It was thought that something ought to be added to the immediate result of the experiment for the loss of heat sustained during its continuance, but the period was so short, that Messrs. Clément and Desormes believed that they indicated its maximum by raising the quantity of the constituent heat of 1 kilogramme of steam to 650 units, their unit of heat being equal to that which is sufficient to raise 1 kilogramme of water one degree of the centigrade thermometer.

The same experiment, repeated on the same quantity of steam, with the same apparatus, the same day, and with an equal quantity of cold water, in fact, under perfectly analogous circumstances, with the sole exception that the steam had different tensions and different temperatures, had precisely the same results as those yielded by the previous experiment. It was far more easy to perceive the similarity than to appreciate any differences that might have presented themselves, and this very circumstance, more than the size of the apparatus and the care directed to the execution of this curious experiment, seems to place the result beyond all doubt.

ficulty of constructing an apparatus capable of resisting such high pressures. It would appear that M. Dulong experienced similar obstacles (see *Cours de Physique*, by M. Lamé, t. i., p. 487, 1e édition).

Mechanicians have in general admitted *Watt's law*, which is very available in calculations, and which moreover appears to be confirmed by the practical observation, that it requires nearly the same quantity of fuel to form one kilogramme of steam, whether at low or high pressure.

M. de Pambour (*Traité de Locomotives, &c.*, 2e édition, chap. ii, and vii) found *Watt's law* confirmed by the experiments which he made on a locomotive. This skilful mechanician observed that steam, when forming in a boiler under an absolute pressure varying from 2·7 to 4·4 atmospheres, and escaping into the atmosphere with an absolute pressure of 1·40 to 1·03 atmospheres, presents precisely the same temperature at the time of its escape, as if it were still in a state of saturation. This circumstance coincides with *Watt's law*, whilst, according to *Southern's law*, the steam should escape at a higher temperature, which would be the same in theory as that possessed by the steam when in the boiler. In order, however, to verify M. Pambour's conclusions in all respects, the steam must be assumed to experience no refrigeration during its passage through the apparatus, but this is a condition which it is extremely difficult to realize even with locomotives; moreover, it must likewise be assumed that the steam enters the engine perfectly *dry*, without the admixture of any liquid particles. This is also a very difficult condition to fulfil, especially in locomotives, owing to the rapid play of the slide valves; and the presence of a very small quantity of liquid water, is sufficient to explain the refrigeration of the steam and its condition of permanent saturation, even assuming *Southern's law* to be correct.

Finally, several authors have tried to demonstrate, *à priori*, the correctness of *Watt's* or *Southern's law*, by basing their arguments on more or less ingeniously conceived physical or mechanical grounds. I will not pause to discuss these speculations, which always depend upon principles open to contest; it is evident that the question, engaging our attention, can only

be decided by direct experiments, and the historical detail that I have given of the results yielded up to the present time, shows that they are inadequate to the solution of the difficulties presented by the subject.

Before I proceed to describe the apparatus which I have employed in the determination of the latent heat of steam at different pressures, it would seem expedient that I should pause for a moment to discuss the method of mixtures, in order to establish the causes of error and uncertainty to be avoided; by which means the object of my mode of arrangement will be better understood.

The apparatus employed for determining latent heat of vapours by the method of mixtures consists, essentially, of a retort A (fig. 2, Plate I.,) containing the liquid whose latent heat of evaporation is to be determined, and a calorimeter C enclosing a worm in which the evaporated liquid may be condensed. The retort communicates with the worm by means of a neck *a b c*, bent at *b*. This neck is made of one rising portion *a b*, disposed in such a manner that vapour condensed within it may fall back into the boiler, and of a descending portion *b c*, which is very short and goes into the worm. The direction changes abruptly at *b;* all the steam which is condensed beyond *b*, falls into the worm, and is considered as having parted with its latent heat to the calorimeter. The condensed liquid remains in a box B placed at the end of the worm, and is made to flow out after the conclusion of the experiment in such a manner that its weight may be determined.

Let:

p be the weight of the liquid condensed in the worm;

P „ „ water of the calorimeter, augmented by the weight of the water, which owing to its capacity for absorbing caloric, is equivalent to the calorimeter and to the worm;

t_0 the initial temperature of the water of the calorimeter;

t_1 the final temperature;

T the temperature of the steam;

c the specific heat of the fluid, that of water being taken as the unit;

λ the latent heat of the steam.

We thus have:

$$p\lambda + pc\,(\mathrm{T}-t_1) = \mathrm{P}\,(t_1-t_0),$$

whence is follows that:

$$\lambda = \frac{\mathrm{P}\,(t_1-t_0)-pc\,(\mathrm{T}-t_1).}{p}$$

This expression requires, however, several corrections before it can give the actual latent heat sought.

1. The fluid always requires a somewhat long period of time for its distillation, during which the calorimeter loses a certain quantity of heat by radiation, and by the contact of the surrounding air; the final temperature t, will, therefore, be lower than it would have been, if this loss of heat had not taken place.

Rumford proposed to eliminate this cause of uncertainty, by taking the water of the calorimeter at an initial temperature, lower by several degrees than the temperature of the surrounding air, and continuing the passage of the steam until the temperature of the water exceeded that of the air, by the same number of degrees by which it had previously been below it.

The absolute value of the correction would certainly be considerably diminished by this method, but it would not be wholly removed. The quantities of heat gained, or lost in the two parts of the experiment would perhaps be equal, if the refrigeration and the heating were both effected solely by radiation; but they differ in reality when the experiment is made in the air, and especially, when the latter is agitated. Besides, it is only in rare cases, that water can be introduced into the calorimeter at 5° or 6° below the temperature of the free air, without causing a deposit of dew to be formed on the surface of the calorimeter. This dew, by its subsequent evaporation in the course of the experiment, becomes a new source of disturbance.

This correction is generally determined by calculation, applying the law of Newton to the refrigeration of the vessel; that is to say, the rapidity of the refrigeration of the vase is supposed to be proportional to the excess of its temperature above that of the surrounding medium. If we designate the

temperature of the surrounding medium as τ, the variable temperature of the calorimeter as t, and the time as x, we shall have $\frac{d\,t}{d\,x} = A\,(t - \tau)$.

The constant A is determined by direct experiments on the refrigeration of the apparatus.

On dividing the length of the experiment into elements, $\Delta\,x = 1'$, we may suppose t to be constant and equal to its mean value, during n minutes. The value of the correction is therefore:

$$\Sigma\,\Delta\,t = A\,(t - \tau)\,n\,\Delta\,x.$$

The law of Newton would perhaps give this correction with sufficient exactness, if the refrigeration took place in vacuo, or at any rate, in an atmosphere slightly agitated; but it becomes inexact when the air is in a state of agitation, and more especially, when its motion varies at different moments during the experiment. It often even becomes extremely difficult to know what value of τ must be adopted for the temperature of the external air.

I know of no means of determining this correction with precision, and the experiment must therefore be so conducted as to render the correction as small as possible. The most certain means of attaining this result, is by using an apparatus of considerable dimensions. The rapidity with which the calorimeter cools, may also be slightly retarded by placing the vessel within a second one formed of very thin metal, and lined with cotton wool, or swan's down.

2. A second correction, more uncertain even than the first, is produced by the pipe, which carries the steam into the worm, bringing with it at the same time, a certain quantity of heat by conduction. It is impossible, in the ordinary manner of conducting this experiment, to determine this correction with any certainty.

The quantity of disturbing heat thus introduced, varies with the position of the bend b on the pipe. The portion $a\,b$ of the tube may be supposed to be heated by the steam condensed along the walls, and which falls back into the retort. Even supposing that no particle of steam passes beyond the plane

$a\ \beta$, which intersects b, the calorimeter will not the less receive a certain quantity of heat, brought to it by internal communication along the tube $b\ c$.

It is evident that this portion of heat will attain its maximum when the bend b is immediately at the entrance of the calorimeter, and that it will diminish, on the contrary, in proportion as $b\ c$ is lengthened: it would likewise diminish if the tube $b\ c$ were made of a substance, which was a bad conductor of heat.

But on the other hand, if $b\ c$ be of any considerable length, a cause of error arises, which acts in a contrary manner to the former. All the steam that passes beyond the limit $a\ \beta$ is considered as acting upon the calorimeter, but a portion of the heat given off by this steam during its passage into the tube $b\ c$, is lost by radiation, and by contact with the cold external air. This loss of heat is great in proportion to the length of the part $b\ c$ of the tube. It will easily be conceived, that in every experiment made on a definite fluid, there is a position of the bend b, in which the quantity of heat gained by the first cause, and the quantity of heat lost by the second, counteract each other, but it is difficult to determine this position *à priori*.

3. The steam which penetrates into the calorimeter necessarily carries with it particles of fluid. Even if we suppose the steam to be perfectly dry in that part of the boiler where it passes into the neck $a\ b$, it must necessarily experience a refrigeration in traversing this tube, which will determine the precipitation of a part of the steam in a liquid condition. The greater portion of this fluid returns to the boiler along the sides, but an appreciable part remains in a gaseous condition, and is carried into the calorimeter by the current.

The inconvenience of which I have spoken is manifested, especially, at the beginning and the close of the experiment. At the outset the retort contains air: this air is expelled by the steam which is developed, but on its disengagement in passing through the worm, it necessarily brings with it a certain quantity of steam, which is then condensed. The heat yielded by this condensation is not taken into account, since the initial temperature t, is not observed until the distillation has become

very active. Besides, during the first few moments of the distillation, the tube *a b* is not heated, the condensation of the steam is abundant, and much liquid is consequently yielded. The experiment is usually terminated by removing the fire from under the boiler, but the distillation instead of being immediately stopped, is gradually diminished, whilst its last stage is attended by perturbations analogous to those which took place at its commencement.

4. In the experiments that have been made to determine the latent heat of steam under pressures more considerable than those of the atmosphere, steam is developed in a boiler at high pressure; but immediately on its escape from the boiler, this steam falls to the pressure of the atmosphere in the pipe which carries it to the calorimeter. It is difficult to explain what occurs owing to the enormous expansion to which the steam is thus subjected; the result may probably be a considerable loss of heat, especially, when the conducting pipe is very long, and such must inevitably be the case, where a steam-engine is used in the experiment.

It appears absolutely necessary that the steam should be conducted to the worm with the same elastic force which it possesses in the boiler.

5. The water which is collected in the box B of the worm has not precisely the same temperature as the surrounding water of the calorimeter, at the moment when the maximum temperature of the latter is observed. When the experiments are made solely at the pressure of the atmosphere, we may compute the difference of the temperature with sufficient precision, by means of a small thermometer, the bulb of which is placed in the centre of the box B, but this method is not applicable when steam condenses at a high pressure. Having made these preliminary remarks, I shall now proceed to the description of the apparatus.

The most essential parts are,—

1. A boiler, A.

2. A condenser, D.

3. An air receiver, E F, which acts in the place of an artificial atmosphere.

4. A system of two precisely similar calorimeters, C and C′.

5. A cock, R, by which the steam is distributed.

6. A mercury manometer.

7. A forcing air-pump.

1. The boiler consists of a vat made of iron plate, 12 mm. in thickness; the diameter of this vat is about $0^{m}{\cdot}64$, and its height $0^{m}{\cdot}80$. It is surrounded by a ring of cast iron to which the cover of the boiler is attached by means of strong pegs screwed on, and by a joint. The cast iron cover, about 30 mm. in thickness, has two small tubes. The upper tube is closed by a cast iron plate, to which three iron tubes are hermetically attached at their base. These tubes are intended to receive the thermometers employed to indicate the temperature of the steam, and of the water in the boiler. Two of the tubes have an internal diameter of about 10 mm.; the one is carried to the bottom of the boiler, whilst the other does not descend more than half way, and does not reach the level of the water; both are intended to have mercurial thermometers. The third tube, which has an internal diameter of about 30 mm., is made to enclose the bulb of an air thermometer.

The boiler is capable of containing about 300 liters; 150 liters are poured in through an opening in the cover. This aperture is kept closed during the experiment by means of a screw-peg, and an annular lead disk. The boiler must be placed on a brick furnace, which has a high iron-plate chimney, and a register, intended to regulate the draft. The bottom of the boiler and about one decimeter of its lateral walls are alone exposed to the direct action of the fire, in order to prevent the steam being over heated. The fuel generally employed is coke, although a mixture of this substance and pit coal is sometimes used.

A copper tube TT′ enters a tubulure T, and is intended to carry the steam to a regulator R.

It is requisite to take precautions to guard against the condensation of the steam in the conducting pipe, as well as against the escape of the liquid water. The first condition necessary to effect this is to prevent the refrigeration of the conducting pipe, by the surrounding air. For this purpose the apparatus is so arranged, that the steam which is to be carried to the calorimeters is enveloped, during the whole of its passage, by a

dense stratum of steam, which is not otherwise employed in the experiment, but possesses the same temperature as the rest, being drawn from the same boiler.

The pipe which carries the steam to the distributing cock R, and consequently also to the calorimeters, has an internal diameter of 35 mm., and is placed in the axis of the pipe TT′, which is nine centimeters in diameter. The pipe TT′ does not communicate immediately with the regulator R, as may be seen in fig. 5, which gives a sectional view of the regulating cock; but a small tube carries off the steam and conveys it directly to the condenser. The interior tube OO′ (fig. 6, Plate I.,) does not terminate at the tubulure T, but penetrates into the interior of the boiler, passing twice round it in the form of a worm, its opening being in the centre of the steam-receiver of the boiler. Thus the steam which is drawn from the centre of the boiler, passes through a worm four meters in length, round the interior of the boiler; reaching the regulator R without experiencing any cause of refrigeration, since the tube OO′ which it traverses is in the axis of a box filled with steam, having the same temperature.

2. The condenser D is a cylinder made of iron plate, 12 mm. in thickness. It is placed in a large reservoir also made of iron plate, and filled with cold water, which keeps the cylinder constantly at a low temperature. An index for the level of the water is fitted to one of the walls of the condenser, and shows at every moment, the quantity of water which has passed into the condenser, and the manner in which the distillation is proceeding.

The condenser D is capable of containing 60 liters; the surrounding water must be kept at a low temperature, and must consequently be continually renewed. A reservoir X furnishes the water necessary for this purpose.

3. The air receiver E F, is composed of a cylinder made of iron plate, 12 mm. in thickness; the diameter of this cylinder is about $0^{m}{\cdot}72$, its length $1^{m}{\cdot}40$, and its total capacity is consequently about 600 liters. The cylinder is placed in a basin Y, being supported by two iron bars. The air receiver communicates with the forcing air pump, and is connected with the box M.

4. The arrangement of the calorimeters will be more easily understood by a reference to fig. 4, Plate I., which represents a vertical section of one of these instruments, and a portion of the main cock.

The calorimeters consist of two red copper cylinders, having very thin metal covers. A cock *s*, placed at the lowest point of the cylinders, allows of the escape of the water contained within them.

The worm consists of a first bulb A made of red copper, 2 mm. in thickness, into which the steam to be condensed passes directly. The water, as well as the steam that has not been condensed, passes through the tube *gh* into a second bulb B, similar to the first, which has at its lower part a cock r_1 placed on the outside of the calorimeter. The same bulb B has an upper tubulure *a*, by which it is connected with a copper worm passing from the calorimeters along the tube $de\,\gamma_1$. This tube $de\,\gamma_1$ has a band by which the worm may be adjusted to copper tubes, and made to communicate with the box M. The tube $de\,\gamma$ of the worm is maintained in the axis of the calorimeter by a narrow band of copper *b d c*.

An agitator or fan, composed of two disks of fluted copper as seen in fig. 5, Plate I., serves to blend together the strata of the water in the calorimeter during the experiment. The two disks are raised on vertical metallic rods, so arranged that when the agitator is at the lowest part of its course, the lower disk is two centimeters from the bottom of the calorimeter, whilst the upper disk is about half-way. By this means a perfectly equal agitation is procured in both calorimeters.

The whole course of the agitators is equal to the half of the height of the calorimeters.

The same volume of water is introduced into the calorimeters at every experiment, being measured by means of a gauging vessel H.

At the lowest point of the gauging vessel, a cock with three branches is soldered on, so placed, that the water may be conveyed at will to the calorimeter C, or to the calorimeter C′.

5. The cock R, by which the steam is distributed, will best be understood by figs. 6 and 7, Plate I., which represent two of

its vertical rectangular sections, and by fig. 4, Plate I., which shows the mode of its disposition between the two calorimeters C and C′.

This cock is composed of a bronze box, cast in a single piece, and composed of a first annular space *j l n m*, to which the steam passes directly by the pipe O′ O, and a central space *h g i k*, which is slightly conical and serves to enclose a hollow cock *a b d e*, a section of which is given in fig. 8, *Plate*. Two tubes *o*C, and *o′*C′, passing to the same basin, establish the communication between the central space *h g i k* and each of the calorimeters; whilst the hollow cock *a b d e* establishes a communication by the lateral opening O, either with the calorimeter C, or with the calorimeter C′, or allows of the complete interception of the passage of steam into the calorimeters.

The branch of the cock passes into the tubulure B, (fig. 6, Plate I.,) which is hermetically closed by means of a ring of hemp, covered with melted caoutchouc, which is rammed into the space B by means of the screw-peg A. This branch has a handle o_2 *m* (fig. 4), by which the cock is worked.

Considerable difficulty was experienced in connecting the tubulures *o*C and *o′*C′ with the worms, since I required that all the joined parts should be placed in the interior of the calorimeters in order to keep the external parts within small dimensions. The mode of adjustment, which I adopted, will be easily comprehended by figs. 4 and 7.

The tubulures *o*C and *o′*C′ terminate in two joined pieces C*ss′*, passing to the same basin, and supporting one turn of the interior screw and one turn of the exterior one.

The communication with the worm is established by means of this turn of the interior screw. For this purpose, the tube *i i′* of fig. 4, one portion of which is represented by *r q* in fig. 7, terminates in a plane disk, which fits into a rabbet in the interior of the joint C*ss′* at the end of the turn of the screw.

A small twist of hemp steeped in a solution of mastic with red lead and surrounding the tube *q r*, is compressed by means of a nut D against the plane disk, terminating the tube *q r*, and thus effects a hermetical closure.

As the tube $q\,r$ is inclined towards the bulb A, in order to facilitate the flow of the water yielded by the condensation of the steam, it was found necessary to give a similar inclination to the pieces Css'. This circumstances increased the difficulties attending the construction of the part of the apparatus under consideration.

It now remains to join the whole of these pieces to the wall of the calorimeter. This wall has a circular orifice a little larger round than the turn of the external screw of the joint Css'. A ring of greased copper is attached to the exterior of the calorimeter between its side and the disk $s\,s'$. A second ring, similar to the former, is placed upon the inner wall of the calorimeter, and the whole system is tightened by means of an annular nut E E′ which works upon the turn of the external screw of the part Css'. As, however, the partition of the calorimeter is vertical, and the direction of $q\,r$ is inclined, it was found necessary to insert a metallic wedge-shaped ring F F′ between the nut E E′ and the wall of the calorimeter.

This mode of arrangement presented some difficulty, since it was necessary for the parts to be kept hermetically closed under pressures of from 15 to 20 atmospheres, whilst they were traversed by steam having a temperature of 200°. The object of placing all the metallic joined parts in the water of the calorimeters was, however, effected, by which means it was found easy to determine at every moment, whether there was any escape of heat, thus removing a cause of anxiety, that would have existed if these parts had been placed on the exterior, owing to the small quantity of heat which they would have been able to convey to the steam.

6 and 7. The mercurial manometer and the forcing air-pump have been already described in my Memoirs on the compressibility of gases, and on the elastic force of steam.

The manometer communicates with the whole of the apparatus by means of a tube which passes into the tubular box M.

All parts of the apparatus have been constructed in such a manner as to resist a pressure of 20 atmospheres; but the principal difficulty consisted in making the whole completely imper-

vious to the air, and able to resist the access of currents of air, which might pass through the small fissures of the metal, or between the numerous joints which it was impossible to dispense with.

The cylinders of fluted iron plate were frequently moistened externally and internally with a solution of sal ammoniac, and then exposed for more than a month to the oxidising action of the atmosphere. By this means the greater number of the crevices in the fluted joints were closed up by rust.

The apparatus was then finally put together, and air at a pressure of 5 atmospheres was compressed into the interior by means of a forcing air-pump. The basins, calorimeters, &c., &c., were filled with water in order to subject all the parts capable of being put under water to its influence; whilst those portions, which did not admit of being thus submerged, were carefully examined, after being moistened with soap and water. A great number of crevices were thus detected, principally in the iron plate; but it was found easy to fill them up by ramming the metal with a graver. A few chinks were also discovered in the bronze parts of the apparatus, and although they might have been stopped by tin solder, I thought it was most prudent to have new parts cast since they would necessarily be very strongly heated when the apparatus was in use.

The copper tubes had been previously tested in a hydraulic press to 20 atmospheres.

After these preliminary trials the apparatus was again put together, and air introduced into the interior at a pressure of 10 atmospheres, and then left during 24 hours. At the end of that time the column of the manometer had only descended 1 decim.; and this slight diminution of the pressure had in a great measure been occasioned by a depression of the temperature, and probably also by an absorption of oxygen owing to the humidity of the metallic walls. It was otherwise impossible to discover any crevice by means of soap and water.

After this trial, the apparatus was considered fit for use.

I. *Total heat of Steam under the ordinary Pressure of the Atmosphere.*

I will begin by describing the experiments that have been made under the ordinary pressure of the atmosphere, in which case a great part of the apparatus becomes useless.

The apparatus is put in communication with the external air by removing the cock R_4 from the air receiver; it is also left in communication with the mercurial manometer, in order to show that there is no sensible excess of pressure in the apparatus during the distillation.

About 150 liters of water are introduced into the boiler, and two mercurial thermometers are so arranged in the iron tubes, that the column of mercury hardly projects beyond the boiler. These thermometers are observed by means of a horizontal lens.

All the parts of the apparatus which are traversed by the current of steam and exposed to the external air, are enclosed in several folds of flannel and list. This covering has been put round the tube TT′, the distributing cock R with its appendices *i i′* leading to the calorimeters, and finally round the return pipe, which carries the steam to the condenser D.

The distributing cock is so placed that the steam cannot reach any of the calorimeters, but must pass directly to the condenser after having traversed the cock R. The distillation is carried on in this manner for $\frac{3}{4}$ of an hour, or a whole hour, until 20 or 30 liters have been conveyed to the condenser; the air is completely expelled from the boiler, and the different parts of the apparatus are placed in a stable condition of temperature.

The amount of cold water is introduced into the calorimeter and the agitators are made to work. The thermometers of the calorimeters are so arranged that the upper extremities of the columns scarcely project beyond the stoppers, by which they are attached to the cover of the calorimeter, and the degrees are observed by means of horizontal lenses which move along vertical columns.

A preliminary experiment is made, consisting in an observation of the heating which is induced in the course of 5 minutes in each of the calorimeters, whilst the water is being continually

agitated. The temperature of the water of the calorimeters is below that of the air, and consequently tends to rise by contact with the surrounding air; moreover, a certain quantity of heat is constantly yielded to the calorimeters by internal conduction through the appendices $i\,i'$ of the distributing cock. The amount of these two quantities of heat is ascertained by an observation.

This observation, combined with another previously made, with respect to the heating of the calorimeters produced under analogous circumstances—but merely by contact with the air, the boiler not being heated—yields the necessary elements for calculating the quantity of heat which passes by conduction along the appendices $i\,i'$, when the distributing cock is traversed by a current of steam at 100°; so that this element of correction is determined by the other experiments.

The distributing cock is then turned so as to make the steam pass into the calorimeter C; the quantity of the water condensed, being ascertained by the reading of the thermometer of this calorimeter. When the requisite elevation of temperature has been obtained, the cock is closed by being brought into its primitive position; the steam continues to pass through the cock R, but the whole amount enters the condenser D, whilst in the other position of the cock, a portion of this steam passed into the calorimeter C. The proportion of steam which passes into the calorimeter, may however be increased or diminuished at will, and, consequently, also the time required for the water of the calorimeter to rise the same number of degrees. If it be desired to prolong this period, the cock R_1 of the condenser is left entirely open, whilst the distributing cock R is only partially opened. If, on the contrary, it is required that the time should be very short, the cock R_1 is partially closed, and the distributing cock R entirely opened. The total quantity of steam, which passes into the apparatus in a given time, may further be increased or diminished by increasing or diminishing the fire under the boiler.

At the moment the cock R is closed, the time must be noted, and the thermometer of the calorimeter C then immerged in such a manner, that the column may only slightly project beyond the stopper; the temperatures indicated by each of the

thermometers of the two calorimeters being observed from minute to minute. The times at which the observations are made, are indicated by the chronometer which strikes minutes.

The mercury in the thermometer of C becomes stationary after one or two minutes, and it then begins to fall. The readings of this thermometer, as well as of the thermometer of C′, are continued for five minutes.

The water condensed in the calorimeter C is suffered to flow, and is collected in a bulb placed below the cock r_1, and having a thermometer with a very small cylindrical reservoir suspended within it. As soon as the full current ceases to flow, the cock r_1 is closed, the water in the bulb is agitated, and the temperature instantaneously observed. The bulb is placed below the cock, and the reading of the thermometers continued for five minutes. At the end of that time, the cock r_1 is reopened, and the few drops of water that have escaped along the walls are collected again. The small quantity of liquid which moistens the interior walls, is considered as being the same in all the experiments, and, consequently, as forming a part of the apparatus.

The quantity of water collected in the bulb must be weighed in a scale, by an assistant.

The agitator must be continually worked by a uniform motion during this interval, and it must still be moved in the same manner during the second part of the experiment, when the calorimeter C′ is in its turn in operation.

The fuel is replaced in the furnace, and when the distillation has again become regular, which may be observed by the manner in which the level of the water rises in the indicator of the condenser, the thermometers of the calorimeters C and C′ are simultaneously noticed, and the distributing cock R is then replaced in the position in which it conveys the steam into the calorimeter C′. This is managed precisely in the same manner as has already been described in the case of the calorimeter C.

Finally, when the condensed water has been removed from the calorimeter C′, the simultaneous fall of the thermometers of C and C′ is observed during five minutes, this cooling being due to the excess of the temperature of the calorimeters over

the surrounding air, notwithstanding the equal quantities conveyed to them by conduction from the distributing cock R.

We will now consider the means, by which the principal causes of error to which I have already alluded have been obviated in this mode of operation; and how the experiment itself furnishes the elements of the different corrections which I have enumerated.

The object aimed at in the disposition of the interior tube, which conveys the steam to the very centre of the boiler, and then winds in the form of a worm more than four meters along the interior of the boiler, is to avoid the escape of the water projected by the agitation of the liquid in the boiler. This bubbling agitation must, however, be inconsiderable, as the ebullition is effected under a regular pressure, unexposed to those sudden alterations, produced at every moment in the boiler of a steam engine by the play of the slide valves.

A thick investment of vapour passing directly to the condenser, and possessing the same temperature, moreover surrounds and accompanies the efficient steam throughout its whole course, even to the small appendices *i i'*, which communicate with the calorimeters, and are only four centimeters in length. By way of greater security, all the metallic parts are enclosed in a woollen covering of considerable thickness.

Finally, the perturbations of which I have spoken, as necessarily present in the ordinary mode of operation, at the beginning and end of the experiment, do not present themselves here, since this experiment has neither *beginning nor end;* the steam not being brought to the calorimeters until the distillation has become regular, and all the parts have resumed their normal temperature.

When the temperature of the calorimeter is higher than that of the surrounding air, a certain quantity of heat is lost by radiation, and also by contact with the surrounding air, but a small quantity of heat is also gained by internal conduction along the appendices *i i'*, which join the calorimeters to the box enclosing the distributing cock R.

If the law of Newton may be applied with sufficient approximative correctness to the cooling of a body in more or less agitated air, for the small excess of temperature which we

obtain in our experiments, we may represent the sum of the two first quantities of heat by an expression of the form

$$\Delta\theta = \mathrm{A}.\theta.\Delta x, \qquad (1)$$

in which

θ represents the excess of the temperature of the calorimeters over that of the surrounding air:

Δx the element of the time:

A a constant which must be determined by direct experiments.

If, on the contrary, it be necessary to separate these two quantities of heat and to apply to each its own law, we may always set down the quantity of the heat lost by radiation as equal to

$$\mathrm{A}.\theta.\Delta x.$$

The cooling occasioned by the surrounding air will be expressed, according to Dulong and Petit, by the form

$$np^{c}\theta^{1,233}.\Delta x,$$

in which p represents the elasticity of the fluid; the exponent c has the same value for all bodies, but changes from one gas to another; n is constant for the same body, but changes with the nature of the elastic fluid.

In our experiments we may suppose

$$np^{c} = \mathrm{B},$$

B being a constant quantity for the same state of agitation of the air, so that the cooling produced by the surrounding air will simply be

$$\mathrm{B}\,\theta^{1,233}\Delta x.$$

Finally, the quantity of heat yielded by conduction for a constant difference between the temperature of the distributing cock R and that of the calorimeter, is merely proportioned to the time: it is represented by

$$\mathrm{K}\,\Delta x.$$

The first question to be solved is, therefore, to ascertain whether cooling by radiation, and by contact with the surrounding air, may be represented with sufficient exactness by an expression of the form

$$\Delta\theta = \mathrm{A}.\theta.\Delta x,$$

or, if we must have recourse to a more complicated formula, as

$$\Delta\theta = A\theta\Delta x + B\theta^{1,233}.\Delta x = A\theta(1 + \frac{B}{A}\theta^{1,233})\Delta x, \qquad (2)$$

comprising two indeterminate constants, A and $\frac{B}{A}$.

For this end I poured water, at higher and higher temperatures, into the calorimeters, and observed the cooling experienced simultaneously by the thermometers of the two calorimeters at 30′; the water being continually agitated. The rapidity of the refrigeration was assumed to be uniform during this interval of time, whilst the temperatures of the calorimeters and the surrounding air were supposed to be equal to the means of those which had been observed at the beginning and end of the 30′, so that the refrigeration for 1′ was obtained by taking the $\frac{1}{30}$ of the total refrigeration obtained.

Number of the Experiments.	Mean Temperatures.			Excess of the Temperatures of the Calorimeters over the surrounding air.		Decrease of the Temperature during 1′.		Value of A in the formula $\Delta\theta = A.\theta.\Delta x.$	
	Of the Air.	Of the Calorimeters.							
		C	C′	C	C′	C	C′	C	C′
1	4°·83	9°·30	9°·95	4°·47	5°·12	0°·00586	0·00646	0·001311	0·001262
2	4·55	8·30	8·87	3·75	4·32	0·00453	0·00498	0·001209	0·001153
3	4·63	11·26	14·74	6·63	10·11	0·00817	0·01298	0·001232	0·001284
4	4·73	14·95	17·90	10·22	13·17	0·01370	0·01897	0·001340	0·001440
5	4·84	19·57	16·89	14·73	12·05	0·01983	0·01779	0·001346	0·001476
						Means		0·001287	0·001338

The two last columns of this table give the values calculated for the co-efficient A in the formula

$$\Delta\theta = A.\theta.\Delta x.$$

It will be observed, that these values are not identical, they do not, however, differ very much, if their extreme absolute smallness be taken into account.

We may apply to these experiments the more complicated formula

$$\Delta\theta = A\theta(1 + \frac{B}{A}\theta^{1,233})\Delta x,$$

calculating the two constants, A and $\frac{B}{A'}$, according to two of the observations, and see whether the three others give the same value for A. I have thus found that the second formula does not represent the observations better than the former, and that the differences are owing much less to the inexactitude of the formula (1) than to the changes which occur in the state of the agitation of the air, and which cause the co-efficients to vary in a very marked manner.

Several other series of observations, made in the same manner, have led to the same result; the variations of A were not sensibly greater when the formula (1) was applied to the observations than when the formula (2) was used.

When the calorimeters exhibit a lower temperature than the surrounding air, and, consequently, when they become heated, the co-efficient A of the formula (1) is very different from that which is applied in case the temperature of the calorimeters is above that of the surrounding air. This will be seen by the following table.

Number of Experiments.	Mean Temperature			Excess of the Temperature of the Calorimeters over the surrounding air.		Variation of the Temperature in 1′.		Value of A in the formula $\Delta\theta = A.\ \theta.\ \Delta x.$	
	Of the Air.	Of the Calorimeters.							
		C	C′	C	C′	C	C′	C	C′
1	12°·20	20°·17	7°·98	+7°·97	−4°·22	0°·01114	0°·01005	0°·001398	0·002570
2	12·20	19·78	8·29	+7·58	−3·91	0·01087	0·00913	0·001434	0·002359
						Means		0·001416	0·002465

Thus, the co-efficient A has a much higher value in those experiments in which the temperature of the calorimeter is below that of the surrounding air, than in those in which its temperature is higher.

I think I may conclude from all these observations, that the formula (1) may be adopted in the calculation of the corrections, with the condition that the value of the co-efficient A shall not be fixed, but be determined, as far as possible, in each

experiment by simultaneous observations, conducted under the same conditions of agitation in the air. The general formula which represents the refrigeration during the element of the time, Δx, is, therefore:

$$-\Delta\theta = A\theta.\Delta x - K\Delta x,$$

A and K being co-efficients having special values for each experiment. We shall see how they may be calculated by the experiments themselves.

Let

t_0 be the initial temperature of the water of the calorimeter C,

t_1 the maximum „ „ „

after the passage of the steam.

τ the temperature of the surrounding air,

T the temperature of the steam in the distributing cock R,

t_0' and t_1' the initial and final temperatures of the thermometer of the second calorimeter.

We will consider, at several separate periods, the double experiment which I have already described.

First period.—The two calorimeters are at the temperatures t_0 and t_0' below the temperature τ of the air; steam passes through the distributing cock directly to the condenser. The heating experienced during these circumstances by the two calorimeters during five minutes is then observed. If we assume the element of the time, Δx, to be equal to 1 minute, and designate the $\frac{1}{5}$th of the refrigeration which takes place during 5 minutes by $\Delta\theta$ and $\Delta\theta'$, we have the two equations:

$$\begin{aligned} \Delta\theta &= A(\tau - t_0) + K, \\ \Delta\theta' &= A(\tau - t_0') + K. \end{aligned} \qquad (3)$$

As the two calorimeters have sensibly the same temperature, and are arranged in a symmetrical manner with reference to the distributing cock R, we may suppose that K has the same value in the two equations; which will, therefore, suffice for determining the two constants A and K.

Second period.—The steam passes into the calorimeter C, whose temperature rises to the maximum t_1. The temperature rises nearly regularly whilst the cock R is open, but as soon

as this is closed it only rises very slowly, attaining its maximum at the end of 2 or 3 minutes.

We will divide into three parts the interval of time which passes between the observations of the initial and the final temperatures.

1. The time m during which the water of the calorimeter C rises from the initial temperature t_0 to the temperature τ of the air; the amount of heat gained is represented by

$$m\left(\mathrm{A}\frac{\tau - t^0}{2} + \mathrm{K}\right), \qquad (4)$$

A and K having the values which have been determined by the experiments of the first period. It would, however, be better, to suppose that K alone was known by these experiments, and to determine A by the simultaneous observation of the heating of the calorimeter C′, to which we may apply the formula

$$\Delta\theta' = m\left(\mathrm{A}\frac{\tau - t'_0}{2} + \mathrm{K}\right). \qquad (5)$$

2. The time m_1, which has intervened between the moment when the calorimeter acquired a temperature equal to that of the surrounding air, and the moment when the cock was closed, and when the temperature of the calorimeter is nearly at its maximum t_1. We will here suppose that the cooling is the same as if the excess of temperature had been constantly $\frac{t_1 - \tau}{2}$, when we should have for the cooling,

$$m_1\left(\mathrm{A}_1\frac{t_1 - \tau}{2} - \mathrm{K}_1\right). \qquad (6)$$

A_1 has no longer the same value as in the first part; its value is deduced from observations made during the third period.

With respect to the quantity K_1, we will suppose it to be proportional to the difference of the temperatures of the cock and of the calorimeter, and consequently we shall admit it to be as follows:

$$\mathrm{K}\frac{\mathrm{T} - \frac{t_1 + \tau}{2}}{\mathrm{T} - t_0},$$

K having the same value as before.

3. The time m_2, which intervenes between the closing of

the cock and the observation of the maximum; the refrigeration is represented in this case by

$$m_2\left(\mathrm{A}_1\,(t_1-\tau)-\mathrm{K}\,\frac{\mathrm{T}-t_1}{\mathrm{T}-t_0}\right). \qquad (7)$$

A_1 having the same value as in the preceding experiment, and being calculated from the observations of the third period.

Third period.—The condensed water has been removed from the calorimeter C; the simultaneous refrigeration of the two calorimeters is then observed during five minutes. We thus have for the calorimeter C,

$$\Delta\theta=\mathrm{A}_1\,(t_1-\tau)-\mathrm{K}\,\frac{\mathrm{T}-t'_1}{\mathrm{T}-t_0}, \qquad (8)$$

from which we deduce the value of A_1 required in the formulæ of the second period.

The calorimeter C′ is in conditions very nearly similar to those which occurred in the first period; thus we have

$$\Delta\theta'=\mathrm{A}'\,(t_0'-\tau)+\mathrm{K}. \qquad (9)$$

K may be considered as the remaining constant; A′ will differ but little from A, but it is requisite to deduce its value from the preceding equation, and use it in the following period in which the calorimeter C′ is brought into action.

Fourth period.—The steam passes into the calorimeter C′, the calorimeter C being in a passive state.

The interval of time comprised between the opening of the cock, and the observation of the maximum temperature may be further subdivided into three parts.

1. The time m', during which the water of the calorimeter C′ rises from its initial temperature t'_0 to the temperature τ of the surrounding air; the amount of heat gained during this period is

$$m'\left(\mathrm{A}'\frac{\tau-t_0}{2}+\mathrm{K}\right). \qquad (10)$$

2. The time m'_1, intervening between the moment at which the water of the calorimeter rises to that of the surrounding medium, and that in which the regulator is closed, and the temperature is near its maximum; the loss of heat is repsesented by

$$m'_1\left(\mathrm{A}'_1\,\frac{t'_1-\tau}{2}-\mathrm{K}\frac{\mathrm{T}-\frac{t_1+\tau}{2}}{\mathrm{T}-t'_0}\right). \qquad (11)$$

The value of the co-efficient A'_1 is deduced from the observation of the simultaneous refrigeration of the calorimeter C, which yields the equation,

$$\Delta\theta_1 = A'_1 (t_1 - \tau) - K \frac{T - t_1}{T - t_0}. \qquad (12)$$

3. The time m'_2 which passes between the closing of the regulator and the moment in which the maximum of the temperature of the calorimeter C′ is observed; the loss of heat during this time is

$$m'_2 \left(A'_1 (t'_1 - \tau) - K \frac{T - t_1'}{T - t'_0} \right), \qquad (13)$$

A'_1 having the same value as above.

Fifth period.—The water has been removed from the calorimeter C′; the sinking of the thermometers of the two calorimeters is observed for 5′, both calorimeters containing water at a higher temperature than that of the air. The formulæ which apply in this case to the cooling in 1′ are,

$$\left.\begin{aligned} &\text{for the calorimeter C, } \Delta\theta = A'_1 (t_1 - \tau) - K \frac{T - t_1}{T - t_0}, \\ &\text{„ \quad „ \quad C′, } \Delta\theta' = A'_1 (t_1' - \tau) - K \frac{T - t'_1}{T - t'_0}. \end{aligned}\right\} \qquad (14)$$

These two expressions may serve to calculate new values for A'_1 and K, which may be compared to those previously obtained. It is evident that the values of t_0, t_0', t_1, t_1', τ change in a slight degree during the course of these experiments; in each case they are taken as yielded by direct observation.

Finally, we have already said, that from the moment at which the thermometer of the calorimeter attained its maximum, the same thermometer was observed from minute to minute, until the removal of the water which was yielded by the condensation of the steam. Suppose these observations to be made during m_3 minutes, it is evident that if the water condensed were at the same temperature as the water of the calorimeter, the refrigeration would be the same as in the observations made after the removal of the water: according to which we should have for the refrigeration

$$m_3 \Delta x \left(A_1 (t_1 - \tau) + K \frac{T - t_1}{T - t_0} \right).$$

By deducting from the value of this expression the actual refrigeration observed, we obtain the small quantity of heat yielded by the condensed water to the calorimeter during this interval of time: and this we will represent by q.

We have thus definitively for the small quantities of heat which must be added to the increase of temperature, $(t_1 - t_0)$, $(t'_1 - t_0')$, by direct observation.

for the calorimeter C,

$$\left.\begin{aligned}\Sigma\Delta\theta = &-m\left(\mathrm{A}\frac{\tau - t_0}{2} + \mathrm{K}\right) + m_1\left(\mathrm{A}_1\frac{t_1 - \tau}{2} - \mathrm{K}\frac{\mathrm{T} - \frac{t+\tau}{2}}{\mathrm{T} - t_0}\right)\\ &+ m_2\left(\mathrm{A}_1(t_1 - \tau) - \mathrm{K}\frac{\mathrm{T} - t_1}{\mathrm{T} - t_0}\right) + q.\end{aligned}\right\} \quad (15)$$

for the calorimeter C′,

$$\left.\begin{aligned}\Sigma\Delta\theta' = &-m'\left(\mathrm{A}\frac{\tau - t'_0}{2} + \mathrm{K}\right) + m'_1\left(\mathrm{A}'_1\frac{t'_1 - \tau}{2} - \mathrm{K}\frac{\mathrm{T} + \frac{t'_1+\tau}{2}}{\mathrm{T} - t'_0}\right)\\ &+ m_2\left(\mathrm{A}'_1(t'_1 - \tau) - \mathrm{K}\frac{\mathrm{T} - t'_1}{\mathrm{T} - t'_0}\right) + q'.\end{aligned}\right\} \quad (16)$$

In a word, the principle of this method consists in determining the corrections which must be applied to the calorimeter in *actual operation*, based upon observations simultaneously made on the second calorimeter, which is in a passive condition, that is to say, subject to the same circumstances of external perturbation, with this difference, that it does not receive any steam; so that the variations are only produced by disturbing causes, which act simultaneously on the first calorimeter.

The temperature Θ of the condensed water is observed in the bulb o immediately after its escape from the calorimeters. This temperature always differs, in a slight degree, from the maximum temperature of the calorimeter, but the difference rarely amounts to 1°.

The observed temperature Θ is not absolutely exact; it is evident that it sinks a little during the flow of the water. Some direct experiments, made under circumstances as nearly as possible similar to those existing in actual experiments, have shown that this decrease of temperature varied from 0°·10 to

0°·20, according to the excess of the temperature over the surrounding air. I made this small correction in each case for the observed temperature Θ; the uncertainty resulting from this circumstance is, however, wholly insignificant; and it easy to show, that it cannot induce an error of $\frac{1}{20,000}$ on the latent heat sought*.

It is often necessary in practice, owing to the small value of these corrections, to deviate, in a slight degree from the method that I have described in the calculation of the corrections. Thus the equation 3 and the equation 5 rarely differ sufficiently, in a numerical point of view, to be considered as distinct equations, and to serve for the determination of the two constants, A and K. The same may be said of equations 12 and 14, when compared together. But as we may suppose, without any sensible error, that K is constant for excesses of temperature $T-t$ that vary but inconsiderably, it is best to choose amongst all the equations, deduced from experiments made under the ordinary pressure of the atmosphere, those which appear most suitable for determining this quantity, and adopting the mean of the values deduced from them for all the experiments. In this manner it has been found, that $K=0°·0040$ for a difference of temperature $T-t=88°$.

The value of K being once determined, the equations 3, 5, and 8 yield, in each experiment, the special values of A and A′.

The values of A and A′ oscillate about 0°·0022.

,, A_1 and A'_1 ,, 0°·0014.

* I had proposed to determine directly the difference of temperature $\Theta-t_1$ existing at the moment in which the final temperature of the calorimeter is observed, between the condensed water and the surrounding water. With this view, I placed a thermo-electric element of iron and copper in the centre of the bulb B; the second segment of the element being placed in the water of the calorimeter and the copper thread which connected the two segments passed over a very sensible galvanometer. To effect this, it was, however, necessary to pierce through the bulb B, and close the thermo-electric element hermetically into the opening. This circumstance would not have presented any difficulty, if the apparatus had only been intended for experiments made under the ordinary pressure of the atmosphere, but it required a special joint for experiments made at a high pressure, and my endeavour was to diminish the number of the joints used, as much as possible. I was also apprehensive that the indications of the thermometric element might be inexact under the conditions in which it would have to be placed.

If it were admitted in the formulæ 15 and 16 that the values of A, A_1, and K were constants for all the experiments, we should find for the corrections, values which scarcely differ by 0°·01 from the more exact values obtained by taking into account all the circumstances that I have enumerated.

The weight of the copper calorimeters, with their worms, the agitator, and interior metallic joints, is:

Calorimeter	C	....	....	.... 15,615 grms.
„	C′	....	....	.... 15,542 „

If we admit the specific heat of copper to be $=0{\cdot}0951$ (*Annales de Chimie et de Physique*, 2me série, tome lxxiii., p. 37,) we shall obtain for the value in water:

for the calorimeter	C	....	....	1482·8 grms.
„	C′	....	....	1475·7 „

The quantity of water introduced into the calorimeters for each experiment always presents the same volume, measured by the gauging vessel, H. The weight of the water which fills the vessel to the marked line has been determined by the most carefully conducted experiments.

In a first experiment, this weight was found to be equal to 65,039·4 grms., the temperature of the water being at 12°,06.

In a second experiment, made at a temperature of 12°00, the weight was found to be 65,046·3 grms. I have adopted this second value, which differs but little from the first, and presents greater guarantees for its accuracy.

It was, however, necessary to determine exactly the weight of the water which filled this gauging vessel, at the different temperatures observed during the experiments. It is easy to determine this weight by calculation, when the dilatations of the water and the iron plate are known. The dilatations of the water may be ascertained with precision, by means of the concordant experiments of M. Despretz and M. Pierre. (*Annales de Chimie et de Physique*, 2me série, tome lxx, p. 47, and *Annales*, 3me série, tome xv., p. 350.)

Hitherto, the coefficient of the linear dilatation of the iron plate has alone been determined, and I do not think that the coefficient of cubic dilatation can be deduced from it, so as to apply to an iron plate vessel of great capacity, and whose walls

have only an inconsiderable degree of thickness. I have given, in another Memoir, the object of which is to determine the calorific capacity of water at different temperatures, a series of direct experiments, from which I have obtained for the co-efficient of the cubic dilatation of vessels of galvanised iron plate, the number $\sigma = 0{\cdot}0000305$.

The following table gives, in the first column, the capacity of the gauging vessel at different temperatures; its volume at 0° being supposed equal to 1.

The second column gives the weight of water enclosed at different temperatures in the vessel; the water having the density which it actually manifests at these temperatures.

The third and fourth columns give the weight of the water at different temperatures increased by the value in water of the calorimeters in respect to calorific capacity.

Temperature.	Capacity of the Gauging Vessel.	Weight of the Water enclosed.	Weight of the Water increased by the Value in Water of the Calorimeters.		Differences for 1°.
			Calorimeter C	Calorimeter C′	
°		Grms.			Grms.
0	1·0000000	65045·0	66527·8	66520·7	....
1	1·0000305	65050·4	66533·2	66526·1	+5·4
2	1·0000610	65055·0	66537·8	66530·7	+4·6
3	1·0000915	65058·6	66541·4	66534·3	+3·6
4	1·0001220	65061·1	66543·9	66536·8	+2·5
5	1·0001525	65062·5	66545·3	66538 2	+1·4
6	1·0001830	65063·0	66545·8	66538·7	+0·5
7	1·0002135	65062·4	66545·2	66538·1	−0·4
8	1·0002440	65060·8	66543·6	66536·5	−1·6
9	1·0002745	65059·2	66542·0	66534·9	−1·6
10	1·0003050	65055·5	66538·3	66531·2	−3·7
11	1·0003355	65051·6	66534·4	66527·3	−3·9
12	1·0003660	65046·3	66529·1	66522·0	−5·3
13	1·0003965	65040·7	66523·5	66516·4	−5·6
14	1·0004270	65034·4	66517·2	66510·1	−6·3
15	1·0004575	65026·0	66508·8	66501·7	−8·4

The mercurial thermometers of the calorimeters have been graduated with the greatest care.

A centigrade degree occupies, on the stem of the thermometer of the calorimeter C, a space of $18^{D}{\cdot}7620$; consequently, 1^{D} has the value $0°{\cdot}053283$; whilst, for the calorimeter C′, the

same quantity occupies $18^{D}{\cdot}5800$; and, therefore, 1^{D} has here the value $0^{o}{\cdot}053821$.

It is easy to distinguish with certainty the tenth of these divisions, that is to say, $\frac{1}{200}$ of a centigrade degree, by means of the horizontal lenses with which these thermometers are observed.

I have collected, in the following table, all the experiments that have been made under the ordinary pressure of the atmosphere.

This table consists of 18 columns.

In column 1 are inscribed the numbers of the succession of the experiments.

In column 2 the calorimeter is indicated with which the experiment was made.

Column 3 gives the weight of the water introduced into the calorimeter, increased by the value in water of this calorimeter.

Column 4 gives the initial temperature, t_0, of the water in the calorimeter.

Column 5 its final temperature, t_1, that is to say, its maximum temperature.

Column 6 the observed elevations of temperature, $t - t_0$. These have been corrected, with respect to different causes of perturbation by the method already described.

Columns 7, 8, 9, and 10 give the elements of these corrections.

Column 11 gives the corrected values of $t_1 - t_0$.

Column 12, the weight of the water condensed in the calorimeter.

Column 13, the temperature of this water on its escape from the calorimeter, after the application of the small correction that I have already indicated.

Column 14 gives the elastic force of the steam, deduced from the observation of the barometer in the external air, the values being given in millimeters of mercury.

Column 15 gives the same in atmospheres.

Column 16, the temperature of the steam deduced from the height of the barometer.

Column 17, the temperature of the steam observed on the thermometers of the boiler.

The temperatures observed in column 17 are generally a little higher than those calculated in column 16, this being necessarily the case, since, in order that the distillation of the water may proceed with activity, the elastic force of the steam in the boiler must be a little above the external pressure.

Column 18 gives the total heat yielded by the steam on its condensation to the condition of liquid water, and its subsequent refrigeration to 0°.

The six first must be considered as preliminary experiments, which have purposely been conducted under the most unfavourable circumstances.

Thus, in experiment No. 1, the fire under the boiler was very small; the introduction of steam into the calorimeter C was continued for 21 minutes.

In experiment No. 4, the introduction likewise lasted 22 minutes.

In experiment No. 3, the fire under the boiler was, on the contrary, very large, but the distributing cock R_1 was shut and opened ten times during the experiment, in order to see whether this circumstance would occasion any sensible perturbation during the experiment.

In experiment No. 5, the fire was small, but the cock R_1, which conveys the steam to the condenser, was completely closed, so that all the steam of the boiler passed into the calorimeter.

In experiment No. 6, the cock R_1 was continually opened and closed.

It will be observed that these different circumstances exercised only a very slight influence on the value of the total heat, having merely rendered it a little smaller.

The 38 other experiments gave values, the extremes of which are 635·6 and 638·4.

The general mean is 636·67.

TABLE I.—Experiments under the

Number of the Experiments.	Calorimeters.	Weight of the Water of the Calorimeter.	Initial Temperature t_0.	Final Temperature t_1.	$t_1 - t_0$ Observed.	Mean Temperature of the Air τ.	Time during which the Steam was introduced.	Time intervening before the fall of the Temperature.
1	2	3	4	5	6	7	8	9
		Grms.	°	°	°	°		
1	C	66524·0	12·81	21·53	8·7216	14·61	21′	23′
2	C	66520·4	13·40	24·84	11·4409	16·02	7	12
3	C	66534·4	11·00	22·82	11·8208	13·65	10	13
4	C	66534·4	11·00	21·96	10·9603	11·85	22	24
5	C′	66538·6	6·19	18·28	12·0918	5·12	10	12
6	C′	66538·1	6·96	19·94	12·9847	6·25	10	12
7	C	66523·5	13·00	24·34	11·3414	16·15	10	11
8	C	66523·1	13·09	24·42	11·3303	16·19	11	12
9	C	66523·3	13·05	24·44	11·3967	15·23	18	19
10	C	66522·5	13·27	24·62	11·3524	15·30	19½	20½
11	C	66535·4	10·76	22·48	11·7196	13·15	10	12
12	C′	66527·3	11·02	23·07	12·0554	14·21	8	10
13	C′	66526·2	11·26	23·15	11·8980	14·26	8½	10½
14	C	66534·4	11·00	22·77	11·7675	14·23	9	12
15	C′	66526·2	11·27	21·63	10·3627	14·34	18	20
16	C	66535·2	10·83	22·53	11·7063	12·18	11	13
17	C′	66526·7	11·14	23·80	12·6594	13·28	9	11
18	C′	66527·6	10·91	23·55	12·6453	13·55	9	11
19	C	66533·4	11·23	21·36	10·1317	13·70	12	14
20	C	66534·0	11·05	21·39	10·3422	13·70	15	17
21	C′	66526·2	11·29	24·41	13·1180	13·57	9	11
22	C′	66526·2	11·26	24·39	13·1301	11·93	10½	12
23	C	66535·0	10·88	22·10	11·2214	12·30	8	10
24	C′	66527·0	11·04	23·68	12·6372	12·30	7	9
25	C	66534·9	10·90	22·22	11·3226	12·11	9	11
26	C′	66527·1	11·05	23·21	12·1585	11·97	8	10
27	C	66545·8	6·03	18·79	12·7612	4·33	8	10
28	C′	66545·6	6·30	18·01	11·7089	5·67	10	12
29	C′	66538·5	6·51	19·37	12·8594	6·04	10	13
30	C	66545·3	6·82	19·29	12·4736	6·10	9	12
31	C	66544·2	4·13	16·79	12·6573	3·13	10	12
32	C′	66536·9	4·04	21·97	17·9331	3·68	10	12
33	C	66544·9	4·64	18·03	13·3873	2·66	9½	12
34	C′	66537·9	4·89	19·67	14·7792	2·83	9	13
35	C	66545·6	5·67	18·16	12·4922	4·87	9	11
36	C′	66537·8	4·78	21·06	16·2835	5·40	8½	11
37	C	66545·6	5·64	18·23	12·5908	5·29	11	13
38	C′	66538·6	5·58	20·10	14·5209	5·68	9½	11
39	C	66543·3	3·77	16·98	13·2142	4·12	10	12
40	C′	66537·1	4·04	18·99	14·9542	4·65	9	11
41	C	66544·2	4·12	17·19	13·0703	5· 0	12	14
42	C′	66537·8	4·75	20·32	15·5677	5·52	9½	11
43	C	66545·0	4·81	18·48	13·6724	5·79	9	11
44	C′	66538·4	5·19	19·86	14·6689	6·05	9½	11

ORDINARY PRESSURE OF THE ATMOSPHERE.

Heat by Conduction during 1′.	$t_1 - t_0$ Corrected.	Weight of the Water Condensed.	Temperature of this Water.	Pressure of the Atmosphere.		Temperature of the Steam.		Total Heat of the Steam.
				In millimeters.	In Atmospheres.	Calculated.	Observed.	
10	11	12	13	14	15	16	17	18
°	°	Grms.	°	mm.	Atm.	°	°	
0·0040	8·7441	949·10	21·50	746·52	0·983	99·49	...	633·3
....	11·4829	1255·15	24·80	746·55	0·983	99·49	...	634·1
....	11·8532	1287·88	22·85	767·06	1·009	100·26	100·58	635·2
....	11·0485	1200·79	21·98	765·94	1·008	100·22	100·25	634·0
....	12·1728	1316·85	....	770·13	1·013	100·37	100·09	633·4
....	13·0710	1413·45	....	768·37	1·011	100·31	100·18	635·4
....	11·3471	1231·10	23·71	746·43	0·982	99·49	....	635·8
....	11·3356	1230·10	23·38	745·71	0·981	99·46	....	636·3
....	11·4284	1240·23	23·53	741·29	0·975	99·31	....	636·4
....	11·3744	1233·05	24·16	740·82	0·975	99·28	....	637·6
.. .	11·7391	1272·84	22·37	765·19	1·007	100·19	100·44	636·0
....	12·0794	1308·85	23·00	765·19	1·007	100·19	100·56	636·8
....	11·9100	1287·65	23·03	765·23	1·007	100·19	100·44	638·3
....	11·7908	1275·57	22·85	765·28	1·007	100·19	100·49	637·9
....	10·3542	1121·04	21·63	765·20	1·007	100·19	100·19	635·9
....	11·7613	1274·57	22·22	767·00	1·009	100·26	100·53	635·9
....	12·6883	1371·61	22·38	767·03	1·009	100·26	100·58	637·9
....	12·6666	1369·23	22·61	767·12	1·009	100·26	100·58	637·9
....	10·1540	1099·03	20·92	767·02	1·009	100·26	100·38	635 6
....	10·3599	1120·99	21·00	767·00	1·009	100·26	100·36	635·8
....	13·1368	1425·42	23·81	767·09	1 009	100·26	100·56	636·7
....	13·1702	1425·58	23·00	765·87	1·008	100·22	100·47	637·6
....	11·2514	1213·19	21·45	765·72	1·008	100 22	100·63	638·4
....	12·6904	1376·68	23·67	765·90	1·008	100·22	100·70	636·8
....	11·3640	1230·03	22·00	765·92	1·008	100·22	100·67	636·6
....	12·2085	1321·87	22·85	765·85	1·008	100·22	100·58	637·2
....	12·8426	1384·70	18·79	770·10	1·013	100·37	100·40	636·1
....	11·7818	1266·75	18·00	768·50	1·011	100·32	100·15	636·7
. ..	12·9476	1395·18	19·37	768·47	1·011	100·32	100·13	637·3
....	12·5640	1354·70	19·32	768·32	1·011	100·31	100·20	636·1
....	12·7499	1369·22	16·03	766·19	1·008	100·22	....	635·6
....	18·0644	1956·04	22·37	766·24	1·008	100·22	....	636·9
....	13·5057	1455·09	18·36	767·15	1·009	100·26	....	635·9
....	14·9242	1612·69	20·19	767·23	1·009	100·26	....	635·9
....	12·5778	1357·20	18·89	735·76	0·968	99·09	....	635·7
....	16·3707	1772·29	21·50	735·76	0·968	99·09	....	636·1
....	12·6746	1363·38	18·02	735·09	0·967	99·07	....	636·6
....	14·6091	1575·64	20·19	735·09	0·967	99·07	....	636·9
....	13·2922	1431·45	18·16	742·87	0·977	99·36	....	636·1
....	15·0354	1619·65	19·18	742·87	0·977	99·36	....	636·8
....	13·1655	1413·95	16·86	742·08	0·976	99·33	....	637·3
....	15·6584	1691·20	20·19	742·05	0·976	99·33	....	636·4
....	13·7426	1483·10	19·03	740·53	0·974	99·27	....	635·7
....	14·7505	1590 50	19·75	740·53	0·974	99·27	....	636·8

II. *Total heat of Steam under Pressures greater than the ordinary Pressure of the Atmosphere.*

I have so arranged my apparatus, that the experiments on steam at high pressure might be conducted under circumstances precisely similar to those occuring where the experiment is made on steam engendered under the ordinary pressure of the atmosphere. The pressure of the external air is then replaced by that of an artificial atmosphere, which may be varied at will. This atmosphere has a considerable volume and is kept at a constant temperature, so that its elasticity does not change sensibly during the course of one experiment.

Air is compressed into the receiver E F by a forcing-pump, in order to obtain the pressure desired for the experiment, this pressure being measured by the mercurial manometer. The ebullition of the water in the boiler is as regular as if effected under the ordinary pressure of the atmosphere. These experiments are conducted exactly in the same manner, and I have nothing to add on this subject to the remarks I have already made in the preceding pages. The manometer is observed at two periods during the course of the experiment; the first time some moments after the opening of the cock R, and again some moments after its close. The pressure, under which the steam is distilled, is taken as the mean of these two obsevations, which never differ very much from one another.

The corrections, which it is necessary to adopt for the elevations of teperature observed, are determined in the same manner as in the experiments made under the pressure of the atmosphere. The elements of these corrections are given by the experiments themselves, as has already been remarked.

The water yielded by the condensation of the steam is projected with force, at the moment in which the cock r_1 of the calorimeter is opened, in order to collect this water in the bulb O, in which it is to be weighed. The time occupied by the flowing of the water is very short, and on this account, the water must experience a smaller loss of heat than when the experiments were made at the ordinary pressure of the atmosphere. I have, however, assumed, as in the last experiments, that the water lost about $0°{\cdot}2$ during its passage, because it is

now subject to a new cause of diminution of heat. This cause arises from the steam, while it is condensed in an atmosphere of compressed air, dissolving a larger quantity of this air than it is able to hold in solution when it reaches the bulb. A number of small vesicles of air are disengaged, which render the water turbid for some instants, and necessarily bring with them a certain quantity of heat.

The experiments progress very easily, and with remarkable regularity, up to a pressure of 10 atmospheres, the results presenting the same precision as those yielded by experiments under the pressure of one atmosphere. Above 10 atmospheres the experiments become more difficult of prosecution; it is necessary to keep up a very strong fire under the boiler, the different parts of the apparatus show much strain, and they require constant inspection, in order to make it certain that no flaw exists in any p art.

Every morning, water that had been distilled the evening before was poured into the boiler, the whole with what had remained, amounting to about 150 liters. This quantity of water was found sufficient, by managing the fire properly during the interval of the experiments, to make from four to six consecutive determinations. By making use of distilled water only, the encrustation of the boiler was avoided, which would otherwise have taken place in a short time.

After the last experiment of the day, the cock R_4 of the air-receiver was closed, whilst the water was still in a state of ebullition in the boiler, in order that the air compressed within it might be kept for the next day. The only loss of air was therefore the small quantity contained in the condenser, and in the pipes of the apparatus; this air escaped on the cocks r_1 of the calorimeters being opened. The following morning, the screw-peg was removed from the boiler, and the necessary quantity of water introduced.

When the pressure of the steam exceeds 10 atmospheres, the joints of the apparatus become rapidly deranged, and it is necessary frequently to renew the twist of hemp, steeped in caoutchouc, which is passed round the stem f of the distributing cock, because the hemp is rapidly consumed by the high temperature of the steam. It is also found requisite frequently

to repair the joints connecting the distributing cock to the worms of the calorimeters. These joints are much worn by the violent and sudden variations of temperature to which they are exposed.

The experiments admitted of being prosecuted with perfect success under pressures equal to 14 atmospheres. I even began a series of experiments under a higher pressure, but the boiler was seriously injured, many crevices were found in the joinings of the iron plate, and numerous flaws round the joint L L′ of the cover; it was consequently found necessary to suspend the experiments.

I hoped, however, to be able to obtain determinations under the pressure of 20 atmospheres, by refitting all the joints

TABLE II.—Experiments under Pressures

Number of the Experiments.	Calorimeters.	Weight of the Water of the Calorimeter.	Initial Temperature t_0.	Final Temperature t_1.	$t_1 - t_0$ Observed.	Mean Temperature of the Air τ.	Time during which the Steam was introduced.	Time intervening before the fall of the Temperature.	Heat by Conduction during 1′.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
		Grms.							
1	C	66537·0	10°32	23°77	13°4566	11°38	7¾′	12′	0°00578
2	C	66536·9	10·37	19·72	9·3511	11·65	11	14	0·00578
3	C	66537·4	10·17	21·79	11·6237	11·32	6½	12	0·00578
4	C	66545·8	6·07	18·09	12·0180	4·75	8	11	0·00600
5	C′	66538·5	6·21	21·73	15·5178	5·13	7	9	0·00600
6	C	66545·8	5·94	18·27	12·3270	4·98	10	12	0·00600
7	C′	66538·5	6·23	20·40	14·1684	5·40	9½	11	0·00600
8	C	66527·1	12·35	24·03	11·6756	13·73	6	9	0·00600
9	C	66526·6	12·47	24·28	11·7971	14·12	6	9	0·00600
10	C	66523·0	12·82	24·39	11·5651	15·37	7	10	0·00600
11	C	66523·0	12·79	24·42	11·6343	15·30	6	10	0·00600
12	C	66525·2	12·60	24·22	11·6233	15·73	10	12	0·00600
13	C	66545·4	5·24	18·16	12·9158	4·44	8	11	0·00600
14	C′	66538·5	5·40	19·39	13·9947	5·06	9	11	0·00600
15	C′	66538·7	5·81	21·20	15·3925	5·60	7	9	0·00600
16	C	66545·7	6·11	17·55	11·4399	5·83	9	13	0·00600
17	C′	66538·4	6·38	19·58	13·2069	6·26	10	13	0·00600
18	C	66545·6	5·50	16·94	11·4452	4·97	11	14	0·00600
19	C	66544·9	4·81	16·99	12·1778	4·98	9	12	0·00650
20	C′	66537·1	4·10	16·76	12·6655	5·10	9½	11	0·00650
21	C	66541·4	3·01	16·21	11·1974	4·77	8	12	0·00650
22	C′	66537·9	4·85	17·68	12·8271	4·51	7	9	0·00650
23	C	66534·4	10·99	22·51	11·5238	13·70	6	11	0·00620
24	C′	66538·5	5·40	19·06	13·6634	5·25	7	9	0·00650
25	C	66528·3	12·11	23·85	11·7393	14·01	6	12	0·00620

of the boiler; but the high pressure to which the boiler had long been exposed, had driven the pegs so deep into the cast-iron cover, that it was impossible, even with the greatest exertions, to remove them, the greater part breaking before they could be extracted. The apparatus could not be repaired without very great expense, whilst there would always have been considerable risk in subjecting it to a more considerable pressure.

The pressure of 14 atmospheres, which was employed in these experiments, exceeds, however, very considerably the pressure obtained in a steam-engine, which rarely exceeds 5 or 6 atmospheres.

I have collected in Table II., 73 experiments, made under pressures varying from 1 to 14 atmospheres.

GREATER THAN THAT OF THE ATMOSPHERE.

$t_1 - t_0$ Corrected.	Weight of the Water Condensed.	Temperature of this Water.	Pressure of the Steam.		Temperature of the Steam.		Total Heat of the Steam.	Total heat Subtracting the Temperature of the Steam in column 16.
			In Millimeters.	In Atmospheres.	Calculated by an Air Thermometer.	Observed on the mercurial thermometer.		
(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)
	Grms.		mm.	Atm.				
13°5190	1456·27	24°68	1448·17	1·905	119°25	119°46	642·3	523·0
9·3563	1000·48	19·72	1462·73	1·924	119·60	119·53	641·8	522·2
11·6780	1253·75	22·36	1582·92	2·083	122·17	122·31	642·2	520·0
12·0700	1282·58	18·12	1742·81	2·293	125·2	125·30	643·9	518·7
15·6032	1669·45	21·73	1768·75	2·327	125·5	125·34	643·6	518·1
12·3871	1315·25	18·16	1849·26	2·433	127·2	127·13	644·8	517·6
14·2464	1517·46	20·42	1952·17	2·568	129·0	128·97	645·1	516·1
11·6942	1247·20	25·27	2285·26	3·007	134·4	....	649·0	514·6
11·8112	1262·70	25·27	2273·47	2·991	134·2	....	647·5	513·3
11·5746	1234·23	24·83	2335·18	3·072	135·1	....	648·5	513·4
11·6347	1238·80	24·39	2325·68	3·060	135·0	....	649·1	514·1
11·5833	1235·50	23·96	2340·83	3·080	135·2	....	647·6	512·4
12·9977	1376·53	18·76	2365·94	3·113	135·5	135·54	647·0	511·5
14·0530	1488·95	19·42	2370·32	3·119	135·7	135·65	647·3	511·6
15·4585	1641·90	21·25	2426·85	3·193	136·4	....	647·6	511·2
11·4794	1212·75	17·59	2498·63	3·288	137·5	137·49	647·4	509·9
13·2781	1407·72	19·69	2517·90	3·313	137·7	137·71	647·2	509·5
11·5038	1211·70	16·84	2588·05	3·394	138·6	138·53	648·4	509·8
12·2258	1287·05	17·32	2842·03	3·739	142·0	142·11	649·2	507·2
12·7136	1339·02	17·29	2860·71	3·764	142·2	142·56	648·9	506·7
11·2475	1184·84	16·19	2911·75	3·831	142·5	142·54	647·8	505·3
12·8699	1353·60	17·92	2955·66	3·889	143·4	143·41	650·3	506·9
11·5008	1221·20	22·95	3042·51	4·003	144·3	....	649·4	505·1
13·7108	1445·32	18·74	3049·85	4·013	144·3	144·31	649·7	505·4
11·7345	1246·50	24·54	3116·00	4·100	145·3	....	651·0	505·7

TABLE II.—

Number of the Experiments.	Calorimeters.	Weight of the Water of the Calorimeter.	Initial Temperature t_0.	Final Temperature t_1.	$t_1 - t_0$ Observed.	Mean Temperature of the Air τ.	Time during which the Steam was introduced.	Time intervening before the fall of the Temperature.	Heat by Conduction during 1′.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
		Grms.	°	°	°	°	′	′	°
26	C	66528·0	12·22	24·35	12·1318	14·28	6	11	0·00620
27	C	66527·6	12·26	24·55	12·2920	14·36	9	11	0·00620
28	C	66537·8	10·90	22·34	11·4464	13·05	17	20	0·00620
29	C	66531·8	11·58	23·87	12·2920	12·85	8	10	0·00620
30	C	66533·0	11·27	23·56	12·2881	13·98	7¼	13¼	0·00620
31	C	66534·3	11·04	23·33	12·2500	13·80	7	12	0·00620
32	C′	66537·5	4·67	15·59	10·9206	4·11	7½	9	0·00670
33	C	66544·6	4·52	18·66	14·1360	3·78	5½	12	0·00670
34	C	66542·5	3·42	16·20	12·7826	4·73	9	12	0·00700
35	C′	66537·7	4·76	18·01	13·2507	3·73	8	12	0·00700
36	C′	66537·3	4·65	18·81	14·1563	4·14	9¼	11	0·00700
37	C	66543·2	3·71	16·20	12·4869	3·27	7½	11	0·00700
38	C	66544·5	4·37	16·37	12·0073	3·73	7¼	14	0·00700
39	C	66541·0	3·16	16·17	13·0090	3·86	8	10	0·00805
40	C	65542·0	3·36	17·75	14·3864	3·47	7½	13½	0·00805
41	C	66541·4	3·01	17·22	14·2079	3·66	8	11	0·00805
42	C	66544·5	4·43	16·66	12·2284	4·69	6½	9½	0·00810
43	C′	66537·9	4·85	19·22	14·3663	4·68	7¾	11	0·00810
44	C′	66537·5	4·45	14·45	9·9971	4·18	5	8	0·00830
45	C	66545·5	5·42	17·75	12·3270	4·59	6½	10	0·00830
46	C′	66538·6	5·73	19·65	13·9179	4·82	6½	9	0·00830
47	C	66544·2	4·13	17·49	13·3581	3·96	7	10	0·00850
48	C′	66537·5	4·52	19·07	14·5482	4·44	6	10	0·00850
49	C′	66538·7	6·09	17·47	11·3808	4·35	6	11	0·00850
50	C	66545·7	5·69	17·59	11·9034	4·20	7	11	0·00850
51	C′	66537·5	4·47	19·09	14·6249	3·72	5	9	0·00850
52	C	66544·1	4·10	17·02	12·9184	3·36	5	10	0·00850
53	C′	66536·4	3·86	17·71	13·8492	2·26	6½	11½	0·00860
54	C	66543·9	4·00	16·95	12·9531	1·83	6	11	0·00900
55	C	66545·0	4·83	17·74	12·9105	2·46	6½	10	0·00900
56	C′	66538·2	5·06	19·57	14·5118	2·73	7	11	0·00900
57	C	66543·8	3·95	17·97	14·0214	4·55	6½	16	0·00950
58	C	66544·6	4·60	17·92	13·3207	4·82	6½	14	0·00950
59	C′	66538·2	4·98	19·16	14·1818	5·07	6¾	12	0·00950
60	C′	66537·7	4·67	19·55	14·8788	4·90	6	15	0·00950
61	C	66545·4	5·17	18·04	12·8732	6·62	5½	18	0·00950
62	C′	66538·6	6·15	20·31	14·1603	7·37	5¾	18	0·00950
63	C′	66538·6	5·76	19·39	13·6275	7·53	6	15	0·00950
64	C	66545·4	5·17	20·62	15·4521	6·99	6¾	18	0·00950
65	C′	66538·5	5·64	19·82	14·1764	8·04	6½	18	0·01000
66	C	66545·4	5·08	18·98	13·9042	7·23	6	16	0·01000
67	C′	66538·4	5·36	20·20	14·8384	8·87	6½	16	0·01080
68	C	66544·9	4·75	19·01	14·2558	7·72	6½	18	0·01080
69	C′	66538·4	5·36	20·94	15·5785	8·39	6½	18	0·01080
70	C	66545·5	6·61	20·41	13·8029	10·80	6	18	0·01100
71	C	66544·4	7·48	21·68	14·1999	9·90	5¾	21	0·01100
72	C′	66538·4	6·50	22·69	16·1920	10·00	6	21	0·01100
73	C	66545·8	5·93	20·04	14·1093	9·70	5¾	20	0·01100

Continued.

$t_1 - t_0$ Corrected.	Weight of the Water Condensed.	Temperature of this Water.	Pressure of the Steam.		Temperature of the Steam.		Total Heat of the Steam.	Total heat Subtracting the Temperature of the Steam in column 16.
			In Millimeters.	In Atmospheres.	Calculated by an Air Thermometer.	Observed on the mercurial thermometer.		
(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)
	Grms.	°	mm.	Atm.	°	°		
12·1253	1291·00	25·12	3128·00	4·116	145·4	....	649·9	504·5
12·2711	1307·01	24·54	3149·25	4·144	145·6	....	649·1	503·5
11·4335	1208·80	21·79	3223·09	4·241	146·5	....	651·1	504·6
12·2756	1305·50	24·13	3323·69	4·373	147·6	....	649·6	502·0
12·2761	1299·00	24·12	3437·85	4·523	149·0	....	652·8	503·8
12·2523	1296·48	23·96	3565·81	4·692	150·2	....	652·6	502·4
10·9170	1144·95	15·59	3883·14	5·109	153·5	153·62	650·1	496·6
14·2327	1499·90	18·70	3945·55	5·191	154·1	154·34	650·2	496·1
12·7840	1338·14	15·84	4045·13	5·335	155·1	....	651·3	496·2
13·3174	1402·45	18·36	4067·81	5·352	155·2	....	650·0	494·8
14·1941	1490·45	18·59	4068·44	5·353	155·2	155·39	652·0	496·8
12·5336	1313·88	16·42	4070·52	5·357	155·3	....	651·0	495·7
12·1007	1269·90	17·32	4115·06	5·415	155·7	....	651·4	495·7
13·0276	1360·26	15·84	4195·56	5·520	156·5	....	652·9	496·4
14·4533	1518·13	18·16	4268·10	5·616	157·1	....	651·4	494·3
14·2382	1491·04	17·52	4350·09	5·724	157·8	....	652·0	494·2
12·2476	1280·25	16·71	4643·15	6·109	160·3	160·74	653·1	492·8
14·4008	1509·65	18·89	4653·75	6·123	160·4	160·77	653·4	493·0
9·9838	1038·70	14·77	4821·20	6·344	161·8	162·34	654·1	492·3
12·3514	1292·20	17·77	5182·11	6·818	164·6	165·06	653·6	489·0
13·9473	1459·05	19·65	5212·47	6·858	164·9	165·40	655·4	490·5
13·3434	1390·60	17·14	6127·67	8·062	171·6	173·03	655·5	483·9
14·5716	1522·15	19·07	6287·61	8·273	172·6	174·17	655·8	483·2
11·4135	1190·38	17·52	6298·49	8·287	172·6	174·96	655·3	482·7
11·9120	1241·32	17·20	6329·21	8·328	172·8	174·96	655·6	482·8
14·6566	1530·15	19·05	6368·87	8·380	173·1	174·92	656·1	483·0
12·9418	1347·65	17·20	6401·76	8·423	173·4	174·84	656·0	482·6
13·9066	1449·30	17·73	6478·81	8·524	173·9	....	655·9	482·0
12·9904	1353·48	17·60	6483·35	8·530	174·0	....	656·0	482·0
12·9349	1347·95	17·71	6702·83	8·819	175·3	....	656·1	480·8
14·5565	1520·88	19·57	6728·59	8·853	175·5	....	656·1	480·6
14·0992	1457·30	18·59	7350·02	9·671	179·3	....	662·3	583·0
13·4219	1387·83	18·59	7416·65	9·759	179·6	....	662·2	482·6
14·2353	1471·35	19·20	7420·62	9·764	179·6	....	662·7	483·1
14·9825	1552·06	20·00	7465·28	9·822	180·0	....	662·2	482·2
12·9428	1337·88	18·88	8056·49	10·600	183·2	....	662·4	479·2
14·2713	1478·64	20·77	8106·48	10·666	183·5	....	662·8	479·3
13·6712	1413·98	19·75	8131·26	10·699	183·7	....	662·8	479·1
15·5494	1614·90	20·92	8138·24	10·708	183·7	....	661·8	478·1
14·2028	1465·93	20·22	8550·41	11·250	186·0	....	664·5	478·5
13·9510	1440·52	20·42	8563·30	11·267	186·0	....	664·9	478·9
14·8716	1537·38	20·60	8925·38	11·744	187·9	....	664·4	476·5
14·3140	1474·39	19·75	8990·73	11·830	188·2	....	665·6	477·4
15·6185	1617·02	21·73	9004·86	11·848	188·2	....	664·2	476·0
13·8296	1427·75	21·66	10141·52	13·344	193·8	....	666·0	472·2
14·2716	1479·00	22·13	10193·27	13·412	194·2	....	664·3	470·1
16·2719	1585·73	23·33	10332·38	13·595	194·7	....	665·4	470·7
14·1389	1456·67	20·48	10354·84	13·625	194·8	....	666·0	471·2

This table presents the same arrangement as Table I., and we will therefore refer our readers to the explanation given, with reference to the latter. We will only observe, that the elastic forces indicated in column 14, are the heights of the mercury observed on the manometer, and increased by the height of the barometer.

Table II. contains one column more than Table I.; this column, which is headed with the number 19, comprises the numbers obtained by subtracting from the total heat inscribed in column 18, the temperature of the steam given in column 16. We shall require these numbers to compare our exprimental determinations with the results deduced from the law of Southern.

Column 16 comprises the temperature of the steam on the air thermometer, deduced from the elastic forces inscribed in column 14. Column 17 gives the temperatures of the steam, observed directly on the mercurial thermometers, which are arranged in the boiler. These two kinds of temperature necessarily differ from one another, since the two instruments do not admit of being compared together; but on taking into account the different course of the two instruments, it will be found that the temperatures observed are generally very sensibly higher than those deduced from elastic forces. These differences often exceed those which we have remarked in the experiments of Table I., and which were made under the pressure of the atmosphere. This circumstance arises from the fact, that in experiments at a high pressure, the steam of the boiler must present an elastic force considerably superior to the pressure of the air of the receiver, in order to produce a sufficiently abundant distillation. This difference of pressure is besides too small in all cases to exercise any detrimental influence on the correctness of the results.

III. *Total heat of Steam under Pressures below that of the Atmosphere.*

The forcing air-pump used in the preceding experiments is, here replaced by a pneumatic machine, and the air is discharged into the receiver E F, until the degree of pressure is obtained which is required for making the determinations. The expe-

riments are conducted in the same manner as when the steam is engendered under high pressure; but the temperature of the water proceeding from the condensation of the steam, can no longer be directly measured, because the water cannot be made to pass from the calorimeter until air has been introduced into the apparatus. It is necessary to assume that the temperature of the condensed water is in a state of equilibrium with that of the calorimeter, at the moment when the maximum temperature is observed. The error which may result from this hypothesis is, however, made apparent, by watching the refrigeration of the calorimeter during the first ten minutes that succeed the observation of the maximum, and by comparing this refrigeration with that which occurs during the following ten minutes. The difference between the two results observed, gives very nearly the quantity of heat yielded by the condensed water to the water of the calorimeter, and it may be assumed that the temperature of the condensed water is in equilibrium with that of the surrounding air.

After every couple of experiments, the cock R_4 of the air receiver E F is closed, and the air suffered to re-enter into the condenser and the boiler; finally, the water condensed in each of the calorimeters is successively collected in the bulb O, and its weight determined.

The ebullition of water at low pressures is more irregular than under high pressures, being attended by starts and intermissions, and the thermometers of the boiler indicate notable variations of temperature according to the greater or less activity of the distillation. In general, a considerable difference is manifested in these experiments, between the pressure of the steam of the boiler and the air of the artificial atmosphere. As the steam has a very considerable density, it is necessary to conduct it with much rapidity, in order that the experiment may not be continued too long. In these more recent experiments, in the place of coke and coal, I have used charcoal, as being more easy to regulate suitably.

TABLE III.

Number of the Experiments.	Calorimeter.	Weight of the Water of the Calorimeter.	Initial Temperature t_0.	Final Temperature t_1.	$t_1 - t_0$ Observed.	Mean Temperature of the Air τ.	Time during which the Steam was Introduced.	Time intervening before the fall of the Temperature.	Heat by Conduction during 1′.	$t_1 - t_0$ Corrected.	Weight of the Water condensed.	Temperature of this Water.	Pressure of the Steam.		Temperature of the Steam.		Total Heat of the Steam.	Total Heat, after Subtracting the Temperature of the Steam, as given in column 16.
													In millimeters.	In Atmospheres.	Calculated.	Observed.		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)	(19)
											Grms.		mm.	Atm.				
1	C′	66538·2	6°·82	19°·62	12°·8029	8°·66	13′	14′	0°·00350	12°·8361	1390·85	....	488·75	0·643	88°·11	87°·96	633°·4	545°·3
2	C	66545·4	6·65	17·90	11·2534	8·34	13	14	0·00350	11·2771	1219·25	....	483·31	0·636	87·83	87·63	633·1	545·3
3	C′	66737·8	7·20	20·33	13·1362	8·74	12	14	0·00350	13·2044	1444·50	....	449·84	0·592	85·97	86·04	628·4	542·0
4	C′	66538·5	6·40	19·21	12·8109	6·60	11	13	0·00350	12·8977	1404·00	....	437·16	0·575	85·24	85·41	628·6	543·4
5	C	66545·3	6·91	18·64	11·7329	8·55	15	17	0·00350	11·7868	1278·98	....	436·62	0·574	85·20	85·32	631·7	546·5
6	C	66545·6	6·30	17·74	11·4398	6·18	8	9	0·00350	11·4730	1246·65	....	430·92	0·567	84·88	85·68	629·9	545·0
7	C	66540·0	10·61	22·53	11·9221	13·45	12	13	0·00345	11·9472	1310·63	....	401·40	0·528	83·08	83·61	628·9	545·8
8	C′	66534·9	9·05	21·63	12·5847	10·00	11	13	0·00345	12·6276	1378·34	....	394·92	0·519	82·66	82·98	631·0	548·3
9	C	66542·4	8·85	21·05	12·2018	11·76	12	14	0·00340	12·2286	1338·45	....	369·80	0·486	81·03	81·42	628·8	547·8
10	C	66534·4	11·02	22·31	11·2906	13·95	9½	12½	0·00340	11·3202	1243·87	....	363·36	0·478	80·60	83·18	627·7	547·1
11	C	66535·0	10·93	22·14	11·2107	14·26	12	14	0·00340	11·2189	1230·15	....	360·12	0·474	80·37	81·08	628·8	547·8
12	C	66543·5	8·05	19·44	11·3919	8·15	12	14	0·00340	11·4240	1244·23	....	357·13	0·470	80·17	80·63	630·2	550·0
13	C	66543·5	8·03	17·01	8·9862	8·78	16	17	0·00240	9·0240	979·10	....	348·22	0·458	79·55	79·29	630·1	550·5
14	C′	66538·1	7·00	17·67	10·6697	6·41	9	11	0·00340	10·7537	1174·26	....	330·63	0·435	78·28	....	627·0	548·7
15	C	66545·3	6·95	20·20	13·2461	6·00	8	10	0·00340	13·3304	1457·37	....	307·17	0·404	76·50	79·76	628·6	552·1
16	C	66538·1	7·09	20·28	13·1907	7·19	12	13	0·00340	13·2773	1462·02	....	247·07	0·325	71·35	72·60	624·4	553·0
17	C′	66538·2	6·93	18·28	11·3505	6·80	9	15	0·00320	11·4712	1264·00	....	244·55	0·322	71·11	72·85	622·2	551·1
18	C	66545·3	6·93	18·69	11·7649	6·91	12	13	0·00320	11·8348	1294·22	....	238·09	0·313	70·49	71·97	626·9	556·4
19	C	66545·3	6·85	19·17	12·3244	6·60	13	14	0·00320	12·4115	1359·50	....	230·17	0·303	69·70	70·77	626·4	556·7
20	C′	66538·4	6·59	19·12	12·5342	6·63	10	12	0·00320	12·6183	1390·98	....	213·72	0·281	68·01	70·41	622·5	554·5
21	C	66545·5	6·48	18·23	11·7462	6·38	13	14	0·00320	11·8259	1297·23	....	198·10	0·270	66·30	68·03	624·7	558·4
22	C′	66538·4	6·73	19·58	12·8493	7·90	10	12	0·00320	12·9255	1424·83	....	181·47	0·239	64·34	67·78	622·9	558·6
23	C	66545·5	6·58	18·25	11·6743	7·52	12	13	0·00320	11·7109	1284·34	....	170·91	0·224	63·02	65·38	625·5	562·5

Table III. contains 23 experiments, made under pressures varying from $0^{atm.}\cdot 64$, to $0^{atm.}\cdot 22$.

On comparing together the experiments made under nearly the same pressure, it will be seen that the total heat yielded by them, presents somewhat greater differences than those shown in Tables I. and II., but only one of these differences amounts to 4·7, that is to say to about $\frac{1}{150}$ of the total quantity measured.

I have not attempted with my large apparatus to make determinations of the total heat of steam under smaller pressures than $\frac{1}{5}$ of an atmosphere, since the ebullition of water under lower pressures is very irregular, and it is difficult to direct it in such a manner, as to obtain results that may be relied upon with any degree of certainty.

It would, however, be desirable, if the total heat of steam in a state of saturation, at very low pressures, could be ascertained with exactness, since this knowledge is of the highest importance in the study of meteorological phenomena. I have repeatedly made a large number of observations to determine it, but many of the methods which I employed require the knowledge of certain elements which are still involved in much uncertainty.

Instead of determining experimentally the quantity of heat yielded by the condensation of a known weight of steam, at a determined pressure, to the cold water of a calorimeter, I have sought to ascertain the quantity of heat, which a known weight of water, placed in the receiver of a calorimeter, abstracts from this calorimeter when evaporated at a very low pressure.

I have made use, for this purpose, of a small calorimeter made of tin-plate, similar in form to that employed by M. Brix, with the exception that the dimensions of my apparatus are larger than the former. After measuring the exact weight of the calorimeter in a scale, it is again weighed after the introduction of about five grms. of distilled water, into the receiver *e f g h*, by means of a small pipe *t t*. By this means the weight of the water to be evaporated is ascertained with precision. The receiver is then put into communication by means of its tubulure *m n*, with a flask which serves as an air-receiver, and which communicates on the one side with a pneumatic machine, and on the other with a barometrical manometer.

The flask serving as an artificial atmosphere is plunged into a freezing mixture, composed of ice and common salt. When the apparatus is properly arranged, a determined volume of water, whose temperature is known, is poured into the calorimeter, which is again covered, whilst a very sensible small thermometer is so arranged, that the bulb is placed in the axis of the calorimeter.

The observation is begun by noting the advance of the refrigeration, or heating of the water of the calorimeter for five minutes, whilst the water is being continually agitated. In order that the refrigeration may proceed with more regularity, the calorimeter is arranged in the centre of a somewhat larger iron plate vessel, to preserve it from the action of accidental currents of air. It is then rapidly emptied by means of the pneumatic machine, and the elastic force of the internal air is then brought to a determined value, observed on the barometrical manometer, which must necessarily be inferior to the elastic force of the steam, at the temperature of the calorimeter.

The distillation of the water in the receiver *e f g h* of the calorimeter, begins as soon as the steam condenses in the cooled flask. The temperature of the calorimeter, the water of which is continually agitated, is then noted from minute to minute, and the elastic force indicated by the barometrical manometer observed at the same time.

The moment, at which the water of the receiver *e f g h* is completely distilled, is easily ascertained by the sudden stopping of the thermometer in its fall; the temperature continues stationary for a very short time, and then rises slowly, provided the temperature of the water of the calorimeter is below that of the surrounding air. The termination of the distillation is likewise ascertained by the barometrical manometer, owing to the sudden rise of a small quantity of mercury in the column communicating with the apparatus.

The ascent or descent of the thermometer is again observed for 5 minutes. This last observation, combined with that of the refrigeration for the 5 minutes preceding the distillation, gives the elements, by which an exact calculation of the corrections for the final temperature may be made, in order to take into account the loss, or gain of heat experienced by the calori-

meter from the surrounding air, during the whole course of the experiment.

Let M be the weight of the water introduced into the calorimeter, increased by the value in water of the calorimeter itself and of its appendices.

m the weight of the water to be evaporated;

t_0 the initial temperature of the calorimeter;

t_1 the final temperature;

then $t_0 - t_1$ is the decrease in the temperature of the water of the calorimeter owing to the evaporation of the water in the receiver.

The quantity $(t_0 - t_1)$ must be corrected owing to the action of external causes on the calorimeter. The correction was effected in the following manner:

A series of preliminary observations was made on the rapidity of the cooling, or the heating presented by the calorimeter, when filled with water at different temperatures; the external air preserving the same temperature. A graphic curve has been constructed from the data yielded by these experiments, the temperatures of the calorimeter being taken as the abscissæ, and the velocities of the cooling, that is to say, the decrease of temperature experienced in a minute, serving as the ordinates. It has been found that this curve differs but little from a straight line, and it may even be assumed, without any sensible error in the valuation of the correction, that it is actually a straight line.

The direct observation of the cooling of the calorimeter during the 5 minutes preceding the experiment, and the observation of the heating during the 5 minutes succeeding it, give the extreme points of the straight line representing the cooling in each experiment. It will, therefore, be sufficient to take on this line the coolings and heatings experienced by the water every moment of the experiment, indicated by the temperature, which must be noted from minute to minute. The total correction to be applied to $t_0 - t_1$ will be equal to the algebraic sum e of all these partial refrigerations.

We shall have, on designating by X the quantity of heat absorbed by 1 gramme of water, when evaporated under the conditions of the experiment: $m\,\mathrm{X} = \mathrm{M}\,(t_0 - t_1 + e)$.

In order that X may represent what we have termed the *total heat* of steam, it is requisite that the evaporated water m should be introduced into the calorimeter at the temperature of 0°. It has, however, in reality the initial temperature t_0, and consequently the total heat will be $X + t_0$.

The quantity $X + t_0$ presents perfectly well the quantity of heat absorbed by the weight m of water at 0°, in order to be reduced to steam under the conditions in which the evaporation is effected; but the question here arises: is the steam actually developed in a state of saturation, and if so, what is the elastic force or the temperature to which this state of saturation corresponds? These are the true difficulties of the subject, and they do not appear to me to admit of being obviated with any degree of certainty.

We know the elastic force f of the air of our artificial atmosphere, this being yielded by the barometrical manometer; but it is evident, that the steam must have a more considerable tension in the receiver $efgh$, since distillation could not otherwise be effected.

The difference between these two tensions must even be very great, for in order that the experiment may be conducted under favourable conditions of exactness, the distillation must be very rapid and the correction e be limited to a very small fraction of $t_0 - t_1$.

A cause of uncertainty of the same nature exists in our experiments at high pressures, the steam necessarily possessing in the boiler an excess of pressure above the air of the artificial atmosphere; but no sensible error can arise from this circumstance, since the excess of pressure is always an extremely small fraction of the total pressure. The case is different with our actual experiments, in which the difference of pressure may be a considerable fraction of the total pressure, since the latter is very small. It is therefore probable that the elastic force f, observed on the barometrical manometer, is appreciably smaller than the mean pressure F at which the steam has distilled.

Moreover, the steam that issues from the calorimeter, is not in a state of saturation. This steam is in a state of saturation at the moment in which it is developed, and its tension corresponds with the temperature τ, presented at this moment by

the water to be evaporated; but this temperature τ must necessarily be below that of the surrounding air of the calorimeter. The steam, before its escape, becomes again heated against the walls of the receiver of the calorimeter, abstracting from them a small quantity of heat, by which the result is rendered more complicated.

Thus (1) we do not know with certainty the temperature θ to which the saturation of the steam corresponds; this temperature must be somewhat above that corresponding to an elastic force of aqueous vapour, equal to the pressure f of the manometer: and (2) the value of $X + t_0$ must be found somewhat too high, since the steam issues from the calorimeter at a temperature above θ.

It is evident, that these causes of uncertainty would be considerably diminished by bringing the pressure f only a little below the elastic force of the aqueous vapour, oorresponding at every moment to the temperature of the water of the calorimeter; but the distillation is in that case very slow, the experiment lasts a long time, and from that circumstance alone is no longer susceptible of exactness.

I do not, however, think that the different circumstances which I have enumerated can sensibly change the results. With a view of ascertaining this, I conducted my experiments under the most varied circumstances; sometimes, for instance, the distillation of 5 grammes of water was most rapidly effected, being completed in 3 or 4 minutes, whilst the apparatus was only subjected to a very low pressure; at another time, I allowed a higher pressure, and in that case, the distillation of 5 grammes of water required 12 minutes. The causes of perturbation were necessarily much more energetic in the former than in the latter instance; the differences were, however, always very small. I also varied the initial temperature of the water of the calorimeter from 9° to 28°.

I have tried to ascertain whether exact results could be obtained for a very slow distillation, on comparing the rapidity of the refrigeration of the calorimeter whilst the water was being evaporated, with that presented by this calorimeter under the same circumstances when the water was not being distilled; but it appeared to me, that it was impossible to deduce any

certain data from this mode of operation, owing to the great irregularity of the distillation.

It has already been stated that the same volume of water was introduced at each experiment into the calorimeter. The weight of this water varied from 500gr. to 502 gr., between the limits of the initial temperatures t_0 observed during my experiments. To this weight must be added the value in water of the calorimeter and its appendices. This value, determined from the weight of the apparatus and the specific heat of the metal constituting it, was found to be 37gr. 5. I determined this value by direct experiments, and by observations on the changes of temperature experienced by the water of the calorimeter on the addition of a determinate quantity of hot water, whose temperature was known with certainty, or by the fusion of a known weight of ice.

I also found as the mean of a great number of experiments, that the value in water of the calorimeter was 42gr. 3. I have assumed for this value the number 40·0, which is evidently the mean between the value calculated, and that which had been found by direct observation.

I have collected in Table IV. all the experiments made according to this process. No special explanation is requisite for its comprehension, as the elements of which it is composed have been sufficiently explained in the preceding pages.

It is necessary to observe that the experiments included in the following table, were purposely made under the most varied circumstances, which were in many cases unfavourable to the exactness of the results. Smaller variations would certainly have been found for the total heat, if the experiments had always been conducted under similar circumstances.

I do not think that we should deviate very considerably from the truth, by assuming that the total heat of the steam developed in a state of saturation at a pressure of $9^{mm}{\cdot}16$, which corresponds to the temperature of 10°, is equal to 610 units. The total heat for water at 0°, would be only some units below this.

TABLE IV.—Experiments under very Feeble Pressures.

Number of the Experiments. (1)	Weight of the Water evaporated, m. (2)	Weight of the Water of the Calorimeter, M. (3)	Initial Temperature of the Calorimeter, t_0. (4)	Final Temperature of the Calorimeter t_1. (5)	$(t_0 - t_1)$ observed. (6)	$(t_0 - t_1)$ corrected. (7)	Mean pressure at which distillation is effected. (8)	Temperature at which Steam presents the Elastic Force, f. (9)	Duration of the Distillation. (10)	Heat absorbed by the evaporated water, x. (11)	Total Heat, $(x + t_0)$. (12)
	Grms.	Grms.					mm				
1	5·250	542·0	9°·21	3°·55	5°·666	5°·748	4·5	− 0°·2	11′	592·3	601·5
2	5·180	541·8	12·17	6·34	5·834	5·713	3·9	− 2·1	7	596·7	608·9
3	5·127	541·8	12·44	7·16	5·281	5·624	4·6	0	9	593·4	605·8
4	5·170	541·4	15·47	10·09	5·382	5·725	7·7	+ 7·4	10	599·0	614·5
5	5·262	541·3	16·47	10·95	5·517	5·815	8·3	+ 8·5	10	597·0	613·5
6	5·127	541·3	16·17	10·82	5·355	5·642	7·8	+ 7·6	9	595·3	611·5
7	5·178	541·0	18·74	13·26	5·483	5·592	9·0	+ 8·6	11	584·3	603·0
8	5·240	541·0	19·22	13·68	5·544	5·675	10·3	+ 11·8	10	585·9	605·1
9	5·220	541·0	19·21	13·63	5·584	5·738	7·8	+ 7·6	7	594·6	613·8
10	5·252	541·0	20·20	14·60	5·605	5·725	11·9	+ 14·0	11	589·7	609·9
11	5·152	541·0	20·31	14·82	5·490	5·557	10·0	+ 11·4	8	582·4	602·7
12	5·242	540·9	21·48	15·90	5·582	5·744	11·5	+ 13·5	12	592·8	614·3
13	5·271	540·8	21·72	16·01	5·713	5·761	6·6	+ 5·2	5	590·2	611·9
14	5·221	540·8	21·71	16·04	5·666	5·717	5·3	+ 2·0	4	591·3	613·0
15	5·200	540·4	23·05	17·40	5·652	5·694	12·4	+ 14·7	8	592·4	615·4
16	5·250	540·4	23·54	17·85	5·693	5·697	8·3	+ 8·5	4	587·1	610·6
17	5·195	540·3	22·81	18·17	5·638	5·626	8·3	+ 8·5	4	585·9	609·7
18	5·162	540·3	24·09	18·49	5·598	5·605	8·6	+ 9·0	4	587·4	611·5
19	5·216	540·3	24·10	18·43	5·672	5·676	8·5	+ 8·9	4	587·6	611·7
20	5·192	540·1	26·40	21·72	5·679	5·641	13·1	+ 16·6	6	586·7	613·1
21	5·085	540·0	27·57	22·00	5·571	5·523	8·6	+ 8·3	4	586·5	614·1
22	5·207	539·9	28·16	22·45	5·710	5·705	7·2	+ 6·4	3	591·6	619·7

I have endeavoured to obtain the latent heat of steam saturated at low pressures, by another method, which will, I hope, enable me to arrive at this result with much certainty, without its being open to the same objections advanced against the first process. But this method, which I have described at the end of my memoir on hygrometry, (*Annales de Chimie et de Physique*, 3me série, tome XV, p. 227,) requires a knowledge of many data that are still involved in considerable uncertainty. It is necessary, for instance, to know the calorific capacity of the air, and the quantity of heat absorbed by the air during its dilatation. I have, therefore, considered it necessary to determine these two elements by means of new experiments, and it is only when these are concluded that I shall be able to calculate the determinations of the latent heat of steam.

On glancing over the Tables I., II., III., and IV., it will be easy to ascertain whether the experiment verifies either of the two laws, which so equally share the authority of physicists.

According to the law of Watt, the quantity of heat necessary to change a kilogramme of liquid water at 0° into steam in a state of saturation, is the same under all pressures. These quantities of heat are set down in column 18 of the tables, and the numbers representing them must therefore remain constant, or, at any rate, only manifest accidental variations arising from errors in the experiments. These numbers increase with the pressure in a perfectly regular manner from 610, which is the value of the total heat of steam at a pressure of $\frac{1}{100}$ of an atmosphere, to 666, which expresses the same quantity under the pressure of 13·6 atmospheres.

The law of Southern maintains, on the contrary, that the heat obtained by subtracting from the total heat the sensible heat indicated by the thermometer, or that which is ordinarily termed, the latent heat of evaporation, remains constant at all pressures. Column 20 of Tables II. and III., gives the numbers obtained by subtracting from the total heat set down in column 18, the temperature (column 19) which would be indicated by an air thermometer plunged into the steam, this temperature being calculated from the elastic forces of steam, as set down in column 14.

If the law of Southern be correct, the numbers of column

20, in Tables II. and III, must remain constant; but these numbers diminish gradually from 560, which corresponds to the pressure of $\frac{1}{5}$ of an atmosphere, to 471, corresponding to the pressure of 13·6 atmospheres, or even from 600 to 471, if we admit the value 610 — 10, which corresponds to the temperature of 10° deduced from Table IV.

The law of Southern deviates therefore still more than the law of Watt, from the numerical results yielded by direct experiments.

It would now be better to seek the true law, connecting together the total quantities of heat contained in steam in a state of saturation, but I do not believe, that this object can at present be effected with any degree of success from the want of several elements, the knowledge of which, appears to me, to be absolutely necessary to the solution of the problem. It seems essential that we should know the law regulating the densities of aqueous vapour in a state of saturation or non-saturation, at different pressures and different temperatures. These densities are generally calculated by supposing, that for a constant temperature the densities of steam in a state of saturation, or non-saturation, may be calculated according to *Mariotte's law*, and that at the same pressure, but different temperatures, the volumes of non-saturated steam may be determined by admitting that steam dilates for every degree of temperature, be its density what it may, by the same fraction of its volume from zero, as the atmospheric air, during the same interval of temperature, when the density of the latter is equal to the pressure of one single atmosphere.

The different researches that I have published, render it very probable that these hypotheses deviate considerably from the truth; it is, therefore, greatly to be desired that these relations may be established with certainty by means of direct experiments.

The observations included in this memoir give the quantities of heat yielded by a kilogramme of steam in a state of saturation at different pressures, and therefore at different temperatures, when reduced to the condition of water at zero. But it also appears essential that the quantity of heat should be known, which is yielded under similar circumstances by a kilogramme

of steam at *different temperatures and different pressures, when in a state of non-saturation.* This will be the object of a future memoir, to which I purpose subjoining new observations on the specific heat of permanent gases, and on the heat disengaged by compression.

These remarks appear to be absolutely necessary in order to explain, in a rational manner, the physical laws of elastic forces of aqueous vapour at different pressures, and those laws, which connect together the total quantities of heat possessed by the steam under determined circumstances. I purpose reverting to this subject, whenever I may succeed in solving experimentally the problems I have just enounced.

But, whatever the law may be, which connects the total quantities of heat with the temperatures, the extent of my experiments lead me to conclude that it may always be numerically developed, according to the ascending powers of t, and to suppose that it gives $\lambda = A + B\,T + C\,T^2 + D\,T^3 + \ldots$ A, B, C, D... being constant co-efficients.

If we assume $\lambda = A$, we have the law of Watt, the incorrectness of which we have seen demonstrated in the preceding experiments. I have tried whether my experiments might be represented with sufficient precision by means of the formula with two terms: $\lambda = A + B\,T$.

We have admitted, according to the experiments of Table IV., that the total heat, contained in steam in a state of saturation, for the temperature + 10°, was . . . 610 units.

Table III. gives as the total quantity of heat, contained in steam in a state of saturation, at 63° 625 „

According to Table I., the total heat of steam in a state of saturation, at the temperature 100°, is . . . . . 637 „

Finally we see at the end of Table II., that the total heat of steam at 195° of an air-thermometer, is . . . . . 666 „

I have calculated the two constants A and B of the formula by means of the two last observations, that is to say, by means of the values of the total heat at the temperatures of 100° and 195°, and from these data, in which I place perfect confidence, I have found:

$A = 606{\cdot}5$

$B = 0{\cdot}305$; so that the numerical formula is $\lambda = 606{\cdot}5 + 0{\cdot}305, T$.

This formula gives very exactly the total heat for the temperatures of $+ 10°$ and $+ 63°$, thus for $T = + 10°$

we have	$\lambda = 609{\cdot}6$
We have assumed from our experiments .	$\lambda = 610{\cdot}0$
For $T = + 63°$ the formula gives . . .	$\lambda = 625{\cdot}2$
Our experiments have yielded . . .	$\lambda = 625{\cdot}0$

We shall besides see that the numbers, yielded by the formula for the different temperatures at which the experiments of Tables II. and III. were made, never present greater differences from the number found experimentally, than may be ascribed to the probable errors of the observations. We may, therefore, admit that our numerical formula represents all our experimental determinations in a satisfactory manner, and that the experiments are not susceptible of sufficient precision to render it expedient to have recourse to a formula with three terms.

We will therefore provisionally adopt the formula $\lambda = 606{\cdot}5 + 0{\cdot}305\ T$, as expressing the numerical law of the phenomenon, until a more thorough knowledge of the properties of steam shall enable us to establish its true physical law.

According to this formula, the total heat, incorporated in a kilog. of saturated steam at the temperature T, is equal to the quantity of heat yielded by a kilogramme of saturated steam at 0°, in passing into the condition of liquid water at 0°, increased by the product $0{\cdot}305\ T$.

The fraction 0·305 is therefore the *special calorific capacity* of steam, different from the calorific capacities of gases at a constant volume, or at a constant pressure, although intimately related to them. It is the quantity of heat required to raise the temperature of a kilogramme of steam 1° in temperature, whilst at the same time, this steam is compressed so as to keep it in a state of saturation.

I have calculated, by means of this formula, the following Table, in which are comprised the total heats incorporated in saturated steam for every 10° of increasing temperature.

Temperature of the Saturated Steam.	Corresponding Elastic Force.		Total Heat.
	In Millimeters.	In Atmospheres.	
	mm.	Atm.	
° 0	4·60	0·006	606·5
10	9·16	0·012	609·5
20	17·39	0·023	612·6
30	31·55	0·042	615·7
40	54·91	0·072	618·7
50	91·98	0·121	621·7
60	148·79	0·196	624·8
70	233·09	0·306	627·8
80	354·64	0·466	630·9
90	525·45	0·691	633·9
100	760·00	1·000	637·0
110	1075·37	1·415	640·0
120	1491·28	1·962	643·1
130	2030·28	2·671	646·1
140	2717·63	3·576	649·2
150	3581·23	4·712	652·2
160	4651·62	6·120	655·3
170	5961·66	7·844	658·3
180	7546·39	9·929	661·4
190	9442·70	12·425	664·4
200	11688·96	15·380	667·5
210	14324·80	18·848	670·5
220	17390·36	22·882	673·6
230	20926·40	27·535	676·6

SAME TABLE IN FAHRENHEIT DEGREES OF HEAT AND ENGLISH INCHES.

Temperature of the Saturated Steam. (Vapour at the point of condensation.)	Corresponding Elastic Force.		Total Heat. (Latent heat + sensible heat above 32°.)
	In Inches.	In Atmospheres.	
32° F.	0·1811	0·006	1123·70° F.
50	0·3606	0·012	1129·10
68	0·6846	0·023	1134·68
86	1·2421	0·042	1140·16
104	2·1618	0·072	1145·66
122	3·6212	0·121	1151·06
140	5·8578	0·196	1156·64
158	9·1767	0·306	1162·04
176	13·9621	0·466	1167·62
194	20·6869	0·691	1173·02
212	29·9212	1·000	1178·60
230	42·3374	1·415	1184·00
248	58·7116	1·962	1189·58
266	79·9321	2·671	1194·98
284	106·9930	3·576	1200·56
302	140·9930	4·712	1205·96
320	183·1342	6·120	1211·54
338	234·7105	7·844	1216·94
356	297·1013	9·929	1222·52
374	371·7590	12·425	1227·92
392	460·1943	15·380	1233·50
410	560·9673	18·848	1238·90
428	684·6584	22·882	1244·48
446	823·8723	27·535	1249·88

VII.

REPORT.

ON THE ARTIFICIAL FORMATION OF ALKALOIDS.

By M. E. Kopp.

There are few questions more deserving of the attention of chemists and pharmaceutists, and of being made the object of their researches, than the formation of alkaloids.

In a chemical point of view, the alkaloids are remarkable for their composition, for their special properties, both physical and chemical, and for the interesting reactions to which many of them give rise, when exposed to the influence of different agents. Considered medically, the organic bases are distinguished by their energetic properties. They constitute at the same time the most violent and sudden poisons, and the most valuable and heroic remedies. Hence their use in medicine is very extensive, while their price is often exorbitant.

It is more than probable that by studying the mode of their formation, we may in course of time be led to prepare artificially, and at little expence, morphine, quinine, strychnine, &c., so as to render these medicines more available to the poor, and to free ourselves from the necessity of heavy payments to foreign countries.

Moreover, there is no impossibility in the artificial formation of the alkaloids.

During the last few years the chemist has formed a tolerably large number of artificial organic bases, similar in all respects to the natural alkaloids; and without doubt the methods adopted in our laboratories, must be analogous to those employed by nature herself.

The question regarding the mode of formation of the alkaloids is naturally divisible into two heads; the former relating to the formation of the natural organic bases, the latter to the modes of preparing the artificial alkaloids.

The former point is beyond all doubt the most important, but unfortunately our ideas on this point are extremely obscure.

Our knowledge respecting the formation of the natural alkaloids is so imperfect, that it may be plainly asserted that nothing has yet been effected, and that we are ignorant of even the first elements of this investigation.

Can we, in point of fact, tell the period at which the alkaloids first present themselves in the juice of plants? Do we know the substances from which they originate? or the circumstances favouring their development? or the influence of oxygen, water, &c. on their formation?

If then our knowledge respecting this department of science be so imperfect, how ought we to proceed, in order to acquire any information regarding the mode in which the natural organic bases are produced?

To attain this object, three different courses are open to us.

I. *The Study of Chemical Botany.*

This would certainly be of immense service in the solution of the question. It would lead us to examine the composition of plants, especially of those yielding these remarkable principles, in the different phases of their growth and decay.

We should especially select the periods of germination, of the development of the leaves, of that of the flower, and of the maturity of the fruit. We should thus arrive at a knowledge of the principles which are contained in plants in the different phases of their vegetative life; we should know what principles are first formed, which afterwards disappear, and what new ones result from them; and we should be thus led to form conjectures on, if not actually to verify, the nature of the relations existing between the first and the last. An investigation of this nature, extending to all the most important plants, would undoubtedly be rich in new and interesting results.

Such a work would fall within the domain of the pharmaceutist, who, being perfectly familiar with the ordinary modes of

their extraction, could, without any great difficulty, isolate pure and frequently crystallizable principles; if their elementary analysis, and their exact description were beyond the ordinary means at his disposal, any chemist would willingly carry on the examination of the substances thus isolated, and in this manner contribute his share to the advancement of his own science.

The following Table contains all the natural alkaloids yet discovered.

They may be divided into three classes:

1. Those which have been submitted to ultimate analysis.

2. Those which have not yet been analysed, but whose existence seems well established.

3. Those whose existence is problematical.

I.

Cinchonine	$C_{20} H_{12} N O$ $C_{19} H_{11} N O$ (Laurent)
Quinine	$C_{20} H_{12} N O_2$ $C_{19} H_{11} N O_2$ (Laurent)
Aricine	$C_{20} H_{12} N O_3$
Brucine	$C_{22} H_{13} N O_4$ $C_{23} H_{13} N O_4$ (Laurent)
Strychnine	$C_{22} H_{12} N O_4$
Morphine	$C_{34} H_{20} N O_6$ $C_{34} H_{19} N O_6$ (Laurent)
Narcotine	$C_{46} H_{27} N O_{14}$
Codeine	$C_{36} H_{21} N O_6$
Pseudo-morphine	$C_{24} H_{18} N O_{12}$
Atropine	$C_{34} H_{23} N O_6$
Berbeerine	$C_{42} H_{26} N O_{16}$
Bebeerine	$C_{34} H_{20} N O_6$
Cafeine	$C_{16} H_{10} N_4 O_3$ (Payen)
Theine	$C_8 H_5 N_2 O_2$
Chelidonine	$C_{40} H_{20} N_3 O_6$
Cinchovatine	$C_{23} H_{14} N O_4$
Conine	$C_{16} H_{17} N$ $C_{16} H_{15} N$ (Laurent)
Corydaline	$C_{34} H_{22} N O_{10}$
Harmaline	$C_{24} H_{13} N O$
Jervine	$C_{30} H_{23} N O_2$
Menispermine	$C_{18} H_{12} N O_2$
Nicotine	$C_{10} H_7 N$
Piperine	$C_{34} H_{19} N O_6$
Sabadilline	$C_{20} H_{14} N O_6$
Staphysaïne....	$C_{32} H_{23} N O_2$
Theobromine	$C_9 H_5 N_3 O_2$

II.

Delphine	Sanguinarine	Pereïrine
Emetine	Porphyroxine	Jamaïcine
Solanine	Sepeerine	Surinamine
Glaucine	Cissampeline	Cicutine
Aconitine	Thebaïne	Macrophylline
Xanthopicrine	Veratrine	Saracine
Chelerythryne	Digitaline (?)	Hederine

III.

Apirine	Cynapine	Euphorbine
Buxine	Esenbeckine	Fumarine
Carapine	Eupatorine	Guaranine
Crotonine		

Bases derived from Escholzia Californica.

1. A base yielding red salts.
2. A colourless acrid base, soluble in ether.
3. A colourless acrid base, soluble in water, and assuming a violet tint when treated with sulphuric acid.

II. *The Study of the Modes of Preparation of the Artificial Alkaloids.*

As we have already observed, it is probable that some of the modes of procedure employed by the chemist in the laboratory are analogous to those actually occurring in nature.

Attention should be especially paid to those methods which most nearly approximate to those employed by nature, and do not require either a very high temperature, or the influence of very energetic reagents; such, for instance, as give origin to thiosinamine, furfurine, &c.

The comparative and rational examination of these processes appears likely to indicate the course we must follow, in order to prepare artificially the natural alkaloids.

The following are the artificial bases at present known:

Melamine	$C_3 H_3 N_3$
Ammeline	$C_6 H_5 N_5 O_2$
Ammelide	$C_{12} H_9 N_9 O_6$ (Liebig) $C_3 H_2 N_2 O_2$ (Gerhardt)
Aniline	$C_{12} H_7 N$
Leukol Quinoleine	$C_6 H_7 N$ (Gerhardt)

Naphtalidine	$C_{20} H_9 N$
Seminaphtalidine } Naphtidine }	$C_{10} H_5 N$
Theosinnamine	$C_4 H_4 N S$
Sinanine	$C_4 H_3 N$
Sinepoline	$C_7 H_6 N O$
Urea	$C H_2 N O$
Lophine	$C_{23} H_8 N$
Amarine	$C_{21} H_9 N$
Furfurine	$C_{15} H_6 N O_3$
Toluidine	$C_{14} H_9 N$
Narcogenine	$C_{36} H_{19} N O_{10}$
Cotarnine	$C_{26} H_{13} N O_6$
Guanine	$C_{10} H_5 N_5 O_2$
Nicotine	$C_{10} H_7 N$
Sugar of gelatine	$C_4 H_5 N O_4$

The bases derived from harmaline, namely:

1. Porphyrharmine, resulting from the action of alcohol on its granules.

2. Leucoharmine, obtained from the chromate of harmaline.

3. Chrysoharmine, yielded by the action of nitric acid on sulphate of harmaline; and finally animine, odorine, and pyrrhol.

To these we may add,

$C_6 H_9 P$. The phosphorized alkaloid of M. Paul Thenard.

$C_2 H_3 As$. Cakodyl and its oxide.

Cakoplatyl, and the platinised bases of M. Reiset.

But their composition is very different from that of the ordinary alkaloids.

III. *The Study of the Products of Decomposition of the Natural Alkaloids under the influence of different Reagents, and under different circumstances.*

It is a recognized fact in chemistry, that the manner in which a substance undergoes decomposition, and the products it yields, frequently enable us to draw conclusions regarding the mode of its formation, and the course to be pursued in forming it.

But the decomposition must not be accompanied with much violence, if we wish to establish the relations existing between the primary body and the derived products, and the equation illustrating the change that occurs. It unfortunately happens that most of the investigations that have been undertaken, in

relation to the changes which the alkaloids undergo, have in no way come up to these conditions, and consequently possess only a moderate degree of interest.

Such, for instance, are those of Brandes, Leber, Jonas, and André, on the action of chlorine on quinine and cinchonine, by which there are produced a series of imperfectly characterised bodies to which the names thalleiochine, russiochine, and melanochine have been applied; those of M. Rousseau on the transformation of strychnine into strychnic acid by chlorate of potash and sulphuric acid; and the researches of M. Marchand on cinchonetine, quinetine, morphetine, &c.—red bodies arising from the action of peroxide of lead acidulated with sulphuric acid, on the sulphates of cinchonine, quinine, morphine, &c.

In the same way the reactions which give origin to quinoleine, are too energetic to afford any information on the natural composition of the body, which furnishes this artificial base.

The same is possibly the case with regard to the action of nitric acid on brucine. As, however, the reaction takes place in the cold, the disengagement of nitrous ether might perhaps indicate that in brucine there exists a grouping of the elements analogous to that occurring in the composition of alcohol, and hence we might draw the conclusion that it may perhaps be advantageous to employ alcohol in the artificial formation of brucine.

The researches of MM. Wöhler and Blyth on narcotine, are more of the nature we have indicated, as permitting us to see into the intimate constitution of a body.

But the (still unpublished) memoir of MM. Redtenbacher, Rochleder, and Wertheim, promises more important results on the nature and composition of the alkaloids, than any of the memoirs to which I have previously alluded.

In fact, these able chemists have announced the following highly important facts.

Piperine should be considered as a neutral combination of a nitrogenous acid with aniline, formed of 2 eq. of the acid and 1 eq. of aniline.

They have even succeeded in reproducing piperine synthetically by directly combining the acid with the base; narcotine

has been separated into a non-nitrogenous acid combined with a peculiar base.

Narcogenine is a combination of this same base with half an equivalent of the acid.

These combinations of the alkaloids are constituted with perfect regularity, containing 1 eq. of water inseparable from the ammonia and the organic alkalies.

It must be apparent that most of the alkaloids, having very high equivalents, thus admit of separation into more simple elements, which, in all probability, will be common to many of them.

The confirmation of this fact would be an important step in the true progress towards our knowledge of the artificial preparation of the alkaloids in general.

Formation of Artificial Alkaloids.

With the view of methodically arranging the modes of preparing the artificial alkaloids, we have united them into groups which embrace in every instance those bases whose formation presents any points of analogy.

But as the same alkaloid may belong equally to several groups, and as, further, it may sometimes be produced under special circumstances, on which it would be difficult to generalize, each base has been examined specially, and the different reactions, under which it may be produced, are pointed out.

FIRST GROUP.

Transformation of the Ammoniacal Compounds.

1. *Thiosinamine,* a combination of ammonia with the essence of black mustard.
2. *Urea,* a metamorphosis of cyanate of ammonia.
3. *Furfurine,* a metamorphosis under the influence of potash on furfurolamide.
4. *Amarine,* a metamorphosis of hydrobenzamide under similar circumstances.
5. *Melamine, Ammeline,* and *Ammelide,* products of the dry distillation of sulphocyanide of ammonium.
6. *Lophine,* derived from hydrobenzamide.

7. The alkali produced by the action of ammonia on cacotheline.
8. *Aniline,* resulting from the action of heat on phenate of ammonia.

1. *Thiosinamine,* $C_4 H_4 N S$.

On mixing essence of mustard or horse-radish with an excess of a concentrated aqueous solution of ammonia in a closed vessel, the essence is gradually transformed into a beautiful crystalline mass which is thiosinamine:

$$\underset{\text{Ess. of mustard.}}{C_8 H_5 N S} + \underset{\text{Ammonia.}}{N H_3} = \underset{\text{Thiosinamine.}}{2 (C_4 H_4 N S)}$$

This alkaloid presents the most simple formation of any.

2. *Urea,* $C H_2 N O$.

An aqueous solution of a combination of hydrated cyanic acid with ammonia, becomes transformed on the least elevation of temperature, or by concentration even at an ordinary temperature, into urea:

$$\underset{\text{Hydrated cyanic acid.}}{C_2 N H O_2} + N H_3 = \underset{\text{Urea.}}{2 (C H_2 N O)}$$

But urea is further the result of the alteration that may be effected (by oxidation) in uric acid, and in different substances derived from it.

Thus, for instance, urea may be obtained:

a. By oxidizing uric acid with peroxide of lead ($Pb O_2$), when allantoine and oxalic acid are also simultaneously produced:

$$\left.\begin{array}{l} 2 \text{ at. uric acid} \ldots\ldots C_{10} H_4 N_4 O_6 \\ 2 \text{ „ peroxide of lead} \ldots\ldots Pb_2 O_4 \\ 3 \text{ „ water} \ldots\ldots\ldots\ldots H_3 O_3 \end{array}\right\} = \left\{\begin{array}{l} C_4 H_3 N_2 O_3 \ldots\ldots \text{allantoin.} \\ C_2 H_4 N_2 O_2 \ldots\ldots \text{2 at. urea.} \\ C_4 Pb_2 O_8 \ldots\ldots \text{oxalate of lead.} \end{array}\right.$$

b. By oxidizing uric acid with nitric acid, when at the same we obtain alloxantin:

$$\left.\begin{array}{l} 2 \text{ at. uric acid} \ldots\ldots C_{10} H_4 N_4 O_6 \\ 5 \text{ „ water} \ldots\ldots\ldots H_5 O_5 \\ 1 \text{ „ oxygen} \ldots\ldots\ldots\ldots O \end{array}\right\} = \left\{\begin{array}{l} C_2 H_4 N_2 O_2 \ldots\ldots \text{2 at. urea.} \\ \\ C_8 H_5 N_2 O_{10} \ldots\ldots \text{alloxantin.} \end{array}\right.$$

c. By oxidizing alloxan with peroxide of lead, when carbonic and oxalic acid are at the same time produced:

$$\underset{\text{Alloxan.}}{C_4 H_2 N O_5} + Pb O_2 = C O_2 + C_2 O_4 Pb + \underset{\text{Urea.}}{C H_2 N O}$$

d. By boiling alloxan with hydrated baryta, when at the same time mesoxalic acid is formed:

$$\underset{\text{Alloxan.}}{C_4 H_2 N O_5} + Ba O, H O = \underset{\text{Urea.}}{C H_2 N O} + C_3 O_6 H Ba_2$$

$$C_3 O_6 H Ba_2 = \underset{\text{Hydrated mesoxalate of baryta.}}{(C_3 O_4, Ba_2 O + H O)}$$

e. By treating allantoin with peroxide of lead:

$$\underset{\text{Allantoin.}}{C_4 H_3 N_2 O_3} + Pb O_2 + H O = 2(\underset{\text{Urea.}}{C H_2 N O}) + \underset{\text{Oxalate of lead.}}{C_2 O_4 Pb}$$

f. On decomposing a solution of oxaluric acid by ebullition:

$$\underset{\text{Oxaluric acid.}}{C_3 H_2 N O_8} + H O = \underset{\text{Urea.}}{C H_2 N O} + \underset{\text{Oxalic acid.}}{C_2 H O_4}$$

Although urea does not exhibit an alkaline reaction, it deserves to be classified amongst the best characterized of the most distinctive alkaloids.

It not only combines with acids, frequently forming crystallisable salts, but also with true salts, such as nitrate of silver, chloride of mercury, and chloride of sodium (according to the researches of MM. Werther and Piria); and further it is capable of forming double salts.

In a large number of cases urea forms compounds analogous to those to which ammonia gives rise.

3. *Furfurine*, $C_{15} H_6 N O_3$.

Furfurine is undoubtedly one of the most remarkable of the artificial bases.

In its composition and properties it approximates the most to the well characterised natural alkaloids; the reaction, on which its origin depends, is not only one of high interest, but it is susceptible of generalization, and we do not fear to affirm that some day or other we shall be indebted to it for the dis-

covery of several new alkaloids. In point of fact, there exists a very close analogy, in respect to the mode of formation, between furfurine, amarine, and melamine.

All these bases result from a modification impressed on compounds derived from ammonia (amides, imides) by a dilute boiling solution of caustic potash. The elementary composition of the original matter has not undergone any alteration, but its chemical character has been changed; previously it was neutral, now it has become strongly alkaline.

In the preparation of formic acid from starch, peroxide of manganese, and sulphuric acid, there is formed an oleaginous matter, which was especially noticed by Mr. Stenhouse, and has received the name of furfurol from Mr. Fownes.

Its composition is represented by the formula $C_{15}\ H_6\ O_6$, or more simply by the formula $C_5\ H_2\ O_2$

This oil, when brought in contact with ammonia, becomes transformed into a solid, slightly crystalline substance, insoluble in water:

$C_{15}\ H_6\ O_6$	+	$N\ H_3$	=	$C_{15}\ H_6\ N\ O_3$	+	$H_3\ O_3$
Furfurol.		Ammonia.		Fulfurolamide.		Water.

This new compound possesses all the characters of an acid; by the action of acids on it, an ammoniacal salt is formed, and furfurol is reproduced.

But when boiled with weak caustic potash, furfurolamide is converted into an energetic alkaloid, *furfurine*, having the same composition and the same equivalent number. The only change that has taken place is in the arrangement of the molecules:

$C_{15}\ H_6\ N\ O_3$	=	$C_{15}\ H_6\ N\ O_3$
Furfurolamide.		Furfurine.

4. *Amarine*, $C_{21}\ H_9\ N$.

This alkaloid is formed in exactly the same manner as furfurine. When 2 eq. of ammonia react on 3 eq. of oxide of benzene (hydride of benzoile) water and hydrobenzamide are formed:

$3\ (C_7\ H_3\ O)$	+	$N\ H_3$	=	$C_{21}\ H_9\ N$	+	$H_3\ O_3$
Hydride of benzoile.		Ammonia.		Hydrobenzamide.		Water.

Hydrobenzamide is decomposed by acids into ammonia and hydride of benzoile, but when treated with a weak boiling solution of potash, it becomes converted into amarine, which forms well marked salts with acids, and has the same composition and equivalent number as hydrobenzamide.

5. *Melamine, Ammeline, and Ammelide.*

The consideration of the formation, nature, and composition of these three alkaloids presents several points of extreme delicacy, not only on account of the inherent difficulties of the subject and the varying statements of different chemists regarding it, but further because it has been made the object of a very warm controversy between MM. Liebig, Gerhardt, and Vœlkel.

Without entering at length into these discussions, let us successively examine the different views regarding the formation of the bases in question, and endeavour to apply to their elucidation the new ideas suggested to us by the discovery of furfurine and amarine.

By the dry distillation of sulphocyanide of ammonium, there are given off sulphide of carbon, sulphuretted hydrogen, and ammonia (and consequently the combinations of these bodies), while there remains a grayish residue to which M. Liebig has given the name of melam:

$$2\,(C_2\,N\,S_2,\,H_4\,N) = C_3\,H_3\,N_3 + C\,S_2 + 2\,H\,S + N\,H_3$$

Sulphocyanide of ammonium. Melam.

M. Liebig has assigned to melam the formula $C_{12}\,H_9\,N_{11}$.

The melam thus obtained cannot be a pure substance.

According to M. Gerhardt it is a mixture of melamine and mellon; M. Vœlkel, at first, regarded it as impure poliene: $C_4\,N_4\,H_4$.

Poliene is a substance isomeric with melamine, but neutral or very faintly basic, insoluble in water and in a weak solution of caustic potash.

But in his subsequent attempts to purify his poliene, M. Vœlkel finding that the only constant product was melamine, concluded that these two substances were identical; and he regards melam as a mixture of melamine with glaucene, $C_4\,H\,N_3$, ammelene $C_6\,H_5\,N_3$ (?), and albene, $C_{12}\,H_9\,N_{10}\,O_3$ (?).

It is evident that none of these opinions is exactly correct.

In the first place impure melam cannot contain oxygen, since sulphocyanide of ammonium is devoid of that element; and melam cannot contain any considerable quantity of melamine, in consequence of the marked differences in the properties of those bodies.

Let us now explain the way in which we conceive the reaction to take place, basing our ideas on the fact demonstrated by Vœlkel, that melamine, and the body contained in the melam, can lose ammonia by heat and be converted into glaucene.

$$\underset{\text{4 at. melamine.}}{C_{12}\,H_{12}\,N_{12}} \quad - \quad \underset{\text{3 at. ammonia.}}{H_9\,N_3} \quad = \quad \underset{\text{3 at. glaucene.}}{C_{12}\,H_3\,N_9}$$

On distilling sulphocyanide of ammonium, there remains as a residue a substance which, when pure, is expressed by the formula:

$$C_6\,H_6\,N_6 = 2 \text{ at. } C_3\,H_3\,N_3$$

and which constitutes pure melam (poliene?).

But too high a temperature may alter a certain quantity, and liberating some ammonia may given rise to a corresponding quantity of glaucene.

(Mellon, which may contain crude melam, must arise from a more advanced decomposition which especially takes place on the walls of the retort).

Hence it may be easily understood that crude melam may give as the result of analysis, the formula $C_{12}\,H_9\,N_{11}$; for, in point of fact:

$$\underset{\text{Pure melam.}}{C_{12}\,H_{12}\,N_{12}} \quad - \quad \underset{\text{Ammonia.}}{H_3\,N} \quad = \quad \underset{\text{Crude melam.}}{C_{12}\,H_9\,N_{11}}$$

Hence crude melam must be a mixture of pure melam with a certain quantity of glaucene.

We regard melam as analogous with furfurolamide and hydrobenzamide.

On submitting it to prolonged ebullition with a weak solution of caustic potash, it gradually undergoes a transformation; from being insoluble and amorphous, it becomes soluble and assumes a crystalline state, and the octohedra, which it finally deposits in the alkaline fluid, consist of a new substance, isome-

ric with that from which it was derived, but possessing also the characters of a tolerably strong alkaloid.

In short the melam is converted into melamine.

Under the prolonged influence of alkalies, and by the action of acids, melamine becomes successively transformed into ammeline, ammelide, and lastly into hydrated cyanuric acid. These changes are induced by the successive loss of one eq. of ammonia which is replaced by two eq. of water. They are expressed by the following equations, which at the same time indicate the relations existing between these different bodies:

$$\underset{\text{Melamine.}}{C_6 H_6 N_6} + 2\,H\,O = H_3 N + \underset{\text{Ammeline.}}{C_6 H_5 N_5 O_2}$$

$$C_6 H_6 N_6 + 4\,H\,O = 2\,H_3 N + \underset{\text{Ammelide.}}{C_6 H_4 N_4 O_4}$$

$$C_6 H_6 N_6 + 6\,H\,O = 3\,H_3 N + \underset{\text{Hydrated cyanuric acid.}}{C_6 H_3 N_3 O_6}$$

Hence we see that melamine, ammeline, and ammelide may be regarded as arising from different cyanurates of ammonia, the mono, bi, and tribasic forms, having lost for each atom of base one atom of water*.

$$\underset{\text{Cyanurate of ammonia.}}{C_6 H_3 N_3 O_6,\ H_3 N} - 2\,H\,O = \underset{\text{Ammelide.}}{C_6 H_4 N_4 O_4}$$

$$\underset{\text{Di-cyanurate of ammonia.}}{C_6 H_3 N_3 O_6,\ 2\,(H_3 N)} - 4\,H\,O = \underset{\text{Ammeline.}}{C_6 H_5 N_5 O_2}$$

$$\underset{\text{Tri-cyanurate of ammonia.}}{C_6 H_3 N_3 O_6,\ 3\,(H_3 N)} - 6\,H\,O = \underset{\text{Melamine.}}{C_6 H_6 N_6}$$

We have adopted Gerhardt's formula for ammelide, for the following reasons:

1. Because the combination of ammelide with oxide of silver, the most distinctive combination that this body is capable of forming, corresponds better with the formula of M. Gerhardt than with that of M. Liebig.

2. Because the formula $C_6 H_4 N_4 O_4$ explains in a better and more simple manner the relations subsisting between the four bodies mentioned.

* Gerhardt, *Précis de Chimie organique.*

3. Because Liebig's formula leads us to admit the existence of a body possessing the singular property of being only capable of combining with 2 at. of acids, 2 at. of oxides, and 2 at. of salts, a circumstance altogether exceptional, and which does not occur in any other body of the class of alkaloids.

For the more complete explanation of this last fact, let us express the bases in question by the notation of equivalents which has latterly been exclusively adopted by Liebig:

Melamine will be expressed by . $C_6 H_6 N_6$
Its combination with acids by . $C_6 H_6 N_6 + \bar{A}$
Its combination with nitrate of silver
by . . . . . $C_6 H_6 N_6 + N O_5, Ag O$
Ammeline will be expressed by . $C_6 H_5 N_5 O_2$
Its combination with acids by . $C_6 H_5 N_5 O_2 + \bar{A}$
Its combination with nitrate of silver
by . . . . . $C_6 H_5 N_5 O_2 + N O_5, Ag O$
Ammelide will be expressed by the
formula . . . . . $C_6 H_{4\frac{1}{2}} N_{4\frac{1}{2}} O_3$

But as a formula cannot contain half-equivalents, we must double it; when we have:

Ammelide . . . . . $= C_{12} H_9 N_9 O_6$
Its combination with acids
will be . . . . . $C_{12} H_9 N_9 O_2 + 2 \bar{A}$
And the combination with
nitrate of silver . . . $C_{12} H_6 N_9 O_6 + 2(N O_5, Ag O)$.

Ammelide may also be developed under the following circumstances:

On exposing nitrate of ammeline to the action of heat, water and protoxide of nitrogen are simultaneously liberated.

$$\underset{\text{Nitrate of Ammeline.}}{C_6 H_5 N_5 O_2} + N H O_6 = \underset{\text{Ammelide.}}{C_6 H_4 N_4 O_4} + 2 N O + 2 H O.$$

By the dry distillation of urea,

$$\underset{\text{16 at. urea.}}{C_8 H_{16} N_8 O_8} = 2 C O_2 + 4 H_3 N + \underset{\text{Ammelide.}}{C_6 H_4 N_4 O_4}$$

MM. Laurent and Gerhardt have further announced that ammelide occurs in the residue of the calcination of hydro-persulphocyanic acid. These able chemists meant to imply that ammelide was one of the products of the action of potash on this residue.

M. Liebig has very rationally observed, that a body not containing oxygen, cannot, when decomposed by heat, yield, as a product, a compound containing oxygen.

6. *Lophine*, $C_{23}\ H_8\ N$.

On heating hydrobenzamide ($C_{21}\ H_9\ N$), ammonia and a very fluid and odorous oil are first disengaged. When ammonia ceases to be developed, the residue left in the retort must be poured into a mortar, and after being exhausted with boiling ether, must be placed in boiling alcohol, into which fragments of caustic potash must be gradually added until perfect solution is effected.

The lophine is deposited as the fluid cools.

This base is also developed in the dry distillation of the mixture obtained by acting on the essence of bitter almonds with sulphide of ammonium.

7. *The Alkaloid derived from Cacotheline.*

It has been shown by MM. Gerhardt and Laurent, that when nitric acid acts on brucine, nitrous ether is liberated, and a peculiar yellow body is formed, to which M. Laurent has given the name of *cacotheline.*

According to this illustrious chemist the reaction is expressed by the following equation.

$$\underset{\text{Brucine.}}{C_{46}\ H_{26}\ N_2\ O_8} + 3\ \underset{\text{Nitric acid.}}{(N\ O_6\ H)} = 2\ \underset{\text{Cacotheline.}}{(C_{21}\ H_{11}\ N_2\ O_{10})} + \underset{\text{Nitrous ether.}}{C_4\ H_5\ N\ O_4} + 2\ H\ O$$

Cacotheline submitted to the action of ammonia is transformed into a new alkaloid, which apparently includes the nitrous vapour.

Its composition has not yet been established.

8. *Aniline*, $C_{12}\ H_7\ N$.

In consequence of its stability, its characteristic properties, the numerous combinations into which it enters, and the highly interesting products to which it gives rise, we may regard aniline as the most important of the artificial bases.

In numerous circumstances its behaviour is similar to that of ammonia, and in many cases the study of aniline will facilitate that of the ammoniacal compounds.

This alkaloid is also produced under extremely various circumstances, and there are many different ways in which it may be formed.

The following are the principal ways in which it may be produced.

1. On decomposing phenate of ammonia by heat, the phenol ($C_6\ H_3\ O$,) combines with ammonia, and the combination heated to 392°F. in a closed tube over a lamp, gives rise to aniline and water.

$$C_{12}\ H_6\ O_2,\ H_3\ N = 2\ H\ O + C_{12}\ H_7\ N.$$

Aniline is then a phenamide, in the same way as melamine, ammeline, and ammelide are cyanuramides.

2. On applying heat to anthranilic acid, it becomes at once decomposed into carbonic acid and aniline. Anthranilic acid is then isomeric with bicarbonate of aniline.

$$\underset{\text{Anthranilic acid.}}{C_{14}\ H_7\ N\ O_4} = 2\ C\ O_2 + \underset{\text{Aniline.}}{C_{12}\ H_7\ N}$$

3. By the decomposition of isatine when acted on, at a high temperature, by hydrate of potash, carbonate of potash is formed, and hydrogen liberated.

$$\underset{\text{Isatine.}}{C_{16}\ H_5\ N\ O_4} + 4\ (K\ O,\ H\ O) = \underset{\text{Aniline.}}{C_{12}\ H_7\ N} + 4\ (K\ O,\ C\ O_2) + H_2$$
$$\text{Potash.}$$

4. By the decomposition of nitro-benzoene, when acted on at a high temperature by carbonate of lime.

$$C_{14}\ H_7\ N\ O_4 = 2\ C\ O_2 + C_{12}\ H_7\ N.$$

5. By the decomposition, under similar circumstances, of salicylamide.

$$\underset{\text{Salicylamide.}}{C_{14}\ H_5\ O_4,\ N\ H_2} = 2\ C\ O_2 + \underset{\text{Aniline.}}{C_{12}\ H_7\ N}$$

6. By the decomposition of nitrobenzide by sulphuretted hydrogen.

$$\underset{\text{Nitrobenzide.}}{C_{12}\,H_5\,N\,O_4} + 6\,H\,S = \underset{\text{Aniline.}}{C_{12}\,H_7\,N} + 4\,H\,O + 6\,S$$

7. In the preparation of M. Mitscherlich's azobenzide, that is to say, in distilling nitrobenzide with an alcoholic solution of potash, there are formed not only aniline and azobenzide but also oxalic acid and water.

$$2\,(\underset{\text{Nitrobenzide.}}{C_{12}\,H_5\,N\,O_4}) + 2\,(\underset{\text{Alcohol.}}{C_2\,H_3\,O}) = \begin{cases} C_{12}\,H_5\,N \text{ azobenzide.} \\ C_{12}\,H_7\,N \text{ aniline.} \\ C_4\,H_2\,O_8 \text{ oxalic acid.} \\ H_2\,O_2 \text{ water.} \end{cases}$$

SECOND GROUP.

Reduction by sulphuretted hydrogen or sulphide of ammonium of nitrogenous combinations, formed from the hydrocarbons, by the substitution of 1 or 2 eq. of nitrous vapour, ($N_2\,O_4$) for 1 or 2 at. of hydrogen.

1. Aniline, by the reduction of nitrobenzide.
2. Nitraniline „ „ binitrobenzide.
3. Toluïdine „ „ nitrobenzoene.
4. Naphtalidine „ „ nitronaphtalide.
5. Seminaphtalidine „ binitronaphtalide.

This mode of forming alkaloids promises a rich future harvest.

We already possess a very considerable number of hydrocarburets, and further so many means of producing them, that science will never be at a loss in furnishing them.

Moreover most of the carburets of hydrogen are attackable by nitric acid, and we shall certainly be able to substitute $N_2\,O_2$ for H_2 of the hydrocarburet.

Having once obtained the compound, all we have to do is to dissolve it in alcohol, and to submit it to the action of sulphuretted hydrogen, or of an alcoholic solution of sulphide of ammonia. Reduction will ensue, and an alkaloid will be found amongst the new products.

The organic bases formed by this method are generally very well characterised, crystallizable, have an alkaline reaction, and readily form crystalline and distinct salts.

They scarcely ever contain oxygen, unless they include the elements of nitrous vapour, (nitraniline).

As the process of formation is absolutely the same for all the different bases of this group, and since, further, (except in the case of aniline,) we do not know of any other method of preparing them, we shall place before our readers the equations illustrating their formation.

It must be remembered that nitrobenzide and binitrobenzide are produced by the action of nitric acid on benzol, (C_{12} H_6); and nitrobenzoene or nitrotoluïde by the action of the same acid on benzoene or toluol (C_{14} H_8); and nitronaphtalide (nitronaphtalese) and binitronaphtalide, (nitronaphtalese) in the same way, from naphthaline (C_{20} H_8).

Reducing by means of sulphuretted hydrogen we have,

$$C_{12}\ H_5\ N\ O_4 + 6\ H\ S = C_{12}\ H_7\ N + 4\ H\ O + 6\ S$$
Nitrobenzide. Aniline.

$$C_{12}\ H_8\ N_2\ O_8 + 6\ H\ S = C_{12}\ (H_6\ N\ O_2)\ N + 8\ H\ O + 6\ S$$
Binitrobenzide. Nitraniline

$$C_{14}\ H_7\ N\ O_4 + 6\ H\ S = C_{14}\ H_9\ N + 4\ H\ O + 6\ S$$
Nitrobenzoine. Toluidine.

$$C_{20}\ H_7\ N\ O_4 + 6\ H\ S = C_{20}\ H_9\ N + 4\ H\ O + 6\ S$$
Nitronaphtalase. Naphtalidine.

$$C_{20}\ H_6\ N_2\ O_8 + 12\ H\ S = 2\ (C_{10}\ H_5\ N) + 8\ H\ O + 12\ S$$
Nitronaphtalise. Seminaphtalide.

Note. Nitrous ether, which has for its formula, C_4 H_5 O, N O_3, or C_4 H_5 N O_4, may be regarded as a hydrocarburet, C_4 H_6, in which an equivalent of hydrogen has been replaced by an equivalent of nitrous vapour, N O_4. If such an arrangement occurred, the action of the sulphuretted hydrogen would, conformably to analogy, be expressed by the following equation:

$$C_4\ H_5\ N\ O_4 + 6\ H\ S = C_4\ H_7\ N + 4\ H\ O + 6\ S$$
Nitrous ether. New alkaloid.

We should obtain the compound C_4 H_7 N, which very probably possesses the characters of an alkaloid.

These are the considerations which have induced me to examine the action of sulphuretted hydrogen on nitrous and nitric ethers.

I. *Reduction of Nitrous Ether by Sulphuretted Hydrogen.*

The nitrous ether was prepared in the manner that I described some years ago in my Chemical Thesis, submitted to the Faculty of Sciences of Strasburgh. It consists in making equal volumes of alcohol and nitric acid react on each other in contact with iron filings or fragments of copper.

The reaction always proceeds quietly, even when operating on considerable quantities, and is almost entirely accomplished without the external application of heat.

The vapour of nitrous ether is first passed through a flask filled with water, for the purpose of washing it; then through a long tube containing chloride of calcium, for the purpose of drying it; and it is finally condensed in a small globular receiver placed in a powerful freezing mixture.

Nitrous ether obtained in this manner is perfectly pure and free from aldehyde.

In fact, on decomposing it by an alcoholic solution of potash, (a decomposition which only takes place slowly,) it remains perfectly colourless. The slightest trace of aldehyde would have given rise to the production of a brown tint.

In this process it is evident that the copper serves to reduce the nitric acid to the state of nitrous acid, by abstracting oxygen from it, and it is the nitrous acid thus developed which reacts on the alcohol.

Nitrous ether is very readily reduced by sulphide of ammonium. The two bodies are hardly in contact before there is an energetic reaction, and in the course of one or two minutes the reduction is complete.

In order to study the products of this reaction, I have adopted two different modes of procedure.

a. An aqueous solution of recently prepared sulphide of ammonium, is introduced into a pretty strong flask with a ground glass stopper; above there is carefully poured a layer of nitrous ether. The flask being well closed, the whole is thoroughly shaken. An energetic reaction instantly occurs, accompanied with the disengagement of heat, and the contents of the flask momentarily assume a brick-red colour, in consequence of the formation of per-sulphide of ammonium. This is immediately followed by decoloration of the fluid and by an abundant precipitation of sulphur.

By successive additions of nitrous ether and sulphide of ammonium, we may readily achieve the complete decomposition of these two bodies.

The precipitated sulphur having been separated by filtration, the liquid is carefully distilled; with the exception of a minute quantity of sulphur, no residue is left in the retort.

The distilled fluid possesses a strong ammoniacal odour. It is neutralized with hydrochloric acid, and again submitted to partial distillation.

The distilled fluid possesses a weak alcoholic, and very slightly alliaceous taste; when heated to the boiling-point the vapour becomes inflammable.

The remaining fluid yields an abundant crystallization of hydrochlorate of ammonia; on concentrating a portion to dryness, it was impossible to detect anything except that salt.

Hence nitrous ether reduced by sulphuretted hydrogen, gives origin to alcohol and ammonia.

$$\underset{\text{Nitrous ether.}}{C_4\,H_5\,N\,O_4} + 6\,H\,S = 3\,\underset{\text{Alcohol.}}{C_2\,H_3\,O} + 2\,H\,O + H_3\,N + 6\,S$$

b. Nitrous ether is dissolved in absolute alcohol, containing a little ammoniacal gas, and a stream of sulphuretted hydrogen is passed through the mixture. A precipitation of sulphur ensues; the distilled fluid yields no residue, the alcoholic fluid in the receiver is ammoniacal, but at the same time possesses an odour of mercaptan.

II. *Reduction of Nitric Ether by Sulphuretted Hydrogen.*

The nitric ether was prepared according to the method described by Millon, was washed with plenty of water, dehydrated and rectified.

Its reduction proceeds much more slowly than that of nitrous ether, and as it is far less volatile, the reaction can be much more easily watched.

On passing a current of sulphuretted hydrogen through nitric ether, diluted with ammoniated alcohol, the mixture begins to boil at between 95° and 104° F. It deepens in colour, and we soon observe minute needles of sulphur deposited at the bottom of the vessel.

They rapidly increase in quantity, and if the nitric ether has not been diluted with alcohol, the whole assumes the character of a half solid magma.

The deposited sulphur is, at intervals, removed by filtration, and the fluid again submitted to the action of sulphuretted hydrogen.

This part of the operation being concluded, we find, that on distilling the alcoholic fluid, no residue is left in the retort, with the exception of a trace of nitrate of ammonia, which is evidently dependent on the regular decomposition of nitric ether by an alkaline base, and a little hyposulphite of ammonia, the latter being the result of the action of the air on an alcoholic solution of hydrosulphuret of ammonia.

In fact, in an imperfectly closed flask containing the last-named substance in solution, we observe that in the course of a few days the fluid becomes colourless, and deposits very thin, magnificent, hexagonal laminæ, forming a considerable surface of very pure hyposulphite of ammonia.

The distilled alcoholic fluid contains ammonia and mercaptan.

The ammonia having been saturated with hydrochloric acid, the fluid, rectified by a fresh distillation, precipitates the salts of lead with a yellow, and the chloride of mercury with a white tint; the precipitate dissolves in boiling alcohol, and reappears on cooling, in the form of brilliant scales.

Nitric ether reduced by sulphide of ammonium, without the intervention of alcohol, also yields mercaptan.

THIRD GROUP.

Distillation of Organic Substances with very Concentrated Hydrate of Potash.

In this group we should place two alkaloids which are ordinarily grouped amongst the natural alkaloids; these are, conine, $C_{16}\ H_{15}\ N$; and nicotine, $C_{10}\ H_7\ N$.

These two bases do not naturally exist in the plants from which we obtain them, but result from the action of hydrate of potash on particular substances or principles, of which that

occurring in tobacco is nicotianine, while that in the Conium maculatum is still unknown.

This reaction is probably similar to that of potash on isatine, which gives rise to aniline.

The alkaloids beloning to this group are:

1. Quinoleine $C_{18} H_7 N$, resulting from the action of hydrated potash, on quinine, cinchonine, and strychnine.
2. Aniline, resulting from the action of potash on isatine.
3. Monochloraniline, derived from chlorisatine.
4. Bichloraniline, derived from bichlorisatine.
5. Monobromaline, derived from bromisatine.
6. Bibromaniline, derived from bibromisatine.
7. Conine, derived from an unknown compound.
8. Nicotine, derived from nicotianine.

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1. *Quinoleine* (Leukol), $C_{18} H_7 N$.

It is only quite recently that M. Gerhardt, to whom science is indebted for the discovery of quinoline, has ascertained that it is identical with a base, leukol, which was previously known, and which is obtained from coal-tar. It occurs together with aniline (kyanol).

It is a fact not devoid of interest that while quinoleine is thus withdrawn from the natural alkaloids already described, aniline may also be obtained from piperine which approximates closely to the alkaloids.

The reactions, giving rise to the formation of quinoleine, are easily expressed by the following equations:

$$\underset{\text{Quinine.}}{C_{19} H_{11} N O_2} = \underset{\text{Quinoleine.}}{C_{18} H_7 N} + C O_2 + H_4$$

$$\underset{\text{Cinchonine.}}{C_{19} H_{11} N O} + H O = \underset{\text{Quinoleine.}}{C_{18} H_7 N} + C O_2 + H_5$$

$$\underset{\text{Strychnine.}}{C_{22} H_{12} N O_2} + 6 H O = \underset{\text{Quinoleine.}}{C_{18} H_7 N} + 4 C O_2 + H_{11}$$

In the dry distillation of coal, the quinoleine is probably formed in a manner analogous to that in which aniline is pro-

duced by the decomposition of a salt corresponding with phenate of ammonia. The following will be the reaction that ensues:

$$C_{18}\,H_6\,O_2 + N\,H_3 = C_{18}\,H_7\,N + 2\,H\,O.$$

2. *Aniline and its derivatives.*

Although we have already given the formula for the production of aniline from isatine and potash, we shall here repeat it in order to shew the identity between its preparation and that of its derivation by substitution.

The chlorine and bromine of chlor- and bromisatine occur as integral portions of chlor- and bromaniline:

$$\underset{\text{Isatine.}}{C_{16}\,H_5\,N\,O_4} + 4\,(K\,O, H\,O) = \underset{\text{Aniline.}}{C_{12}\,H_7\,N} + 4\,(\underset{\text{Carb. potash.}}{K\,O, C\,O_2}) + 2\,H$$
Hyd. potash.

$$\underset{\text{Chlorisatine.}}{C_{16}\,(H_4\,Cl)\,N\,O_4} + 4\,(K\,O, H\,O) = \underset{\text{Chloraniline.}}{C_{12}\,(H_6\,Cl)\,N} + 4\,(K\,O, C\,O_2) + 2\,H$$

$$\underset{\text{Bichlorisatine.}}{C_{16}\,(H_3\,Cl_2)\,N\,O_4} + 4\,(K\,O, H\,O) = \underset{\text{Bichloraniline.}}{C_{12}\,(H_5\,Cl_2)\,N} + 4\,(K\,O, C\,O_2) + 2\,H$$

$$\underset{\text{Bromisatine.}}{C_{16}\,(H_4\,Br)\,N\,O_4} + 4\,(K\,O, H\,O) = \underset{\text{Bromaniline.}}{C_{12}\,(H_6\,Br)\,N} + 4\,(K\,O, C\,O_2) + 2\,H$$

$$\underset{\text{Bibromisatine.}}{C_{16}\,(H_3\,Br_2)\,N\,O_4} + 4\,(K\,O, H\,O) = \underset{\text{Bibromaniline.}}{C_{12}\,(H_5\,Br_2)\,N} + 4\,(K\,O, C\,O_2) + 2\,H.$$

FOURTH GROUP.

Dry Distillation of Organic Matters.

In addition to the well-known alkaloids this group contains some other organic bases which are only imperfectly known; as, for instance, pyrrhol, odorine, and animine, noticed by Unverdorben.

We know scarcely anything of their properties, and still less of their nature and composition.

Dry distillation yields the following alkaloids:

1. Aniline, quinoleine, and pyrrhol by the dry distillation of coal.

2. Odorine and animine by the distillation of animal matters; they ought to be included in Dippel's animal oil.
3. Nicotine by the dry distillation of tobacco.
4. Lophine by the distillation of hydrobenzamide and of the sulphurous products of hydride of benzoile.

FIFTH GROUP.

Decomposition of a Nitrogenous Acid.

This group yields two extremely interesting and remarkable examples: one is the decomposition, by the dry method, of anthranilic acid into carbonic acid and aniline:

$$\underset{\text{Anthranilic acid.}}{C_{14}\,H_7\,N\,O_4} = 2\,C\,O_2 + \underset{\text{Aniline.}}{C_{12}\,H_7\,N}$$

For the second we are indebted to the recent investigations of M. Dessaignes; it is the transformation of hippuric acid into benzoic acid and sugar of gelatine.

Both acids and bases effect this transformation. In consequence of the great analogy between urea and sugar of gelatine we feel compelled to place the latter amongst the alkaloids.

SIXTH GROUP.

Desulphuration of a Sulphuretted Alkaloid.

Under this head we must place the transformation of thiosinamine into sinamine.

Thiosinamine, $C_4\,H_4\,N\,S$, when treated with oxide of lead, reacts as if it were an organic combination of 2 at. of sulphuretted hydrogen with sinamine. Water and sulphide of lead are formed, and the new alkaloid, sinamine, is liberated:

$$\underset{\text{Thiosinamine.}}{C_4\,H_4\,N\,S} + Pb_2\,O = Pb_2\,S + H\,O + \underset{\text{Sinamine.}}{C_4\,H_3\,N}$$

SEVENTH GROUP.

Desulphuration of a Sulphuretted Essential Oil.

The hydrated oxides of lead and mercury, when in contact with the essential oil of mustard, break it up into bisulphide of carbon and into a peculiar alkaloid, sinapoline, whose formula is $C_7\,H_6\,N\,O$.

$$\underset{\text{Essence of mustard.}}{C_8 H_5 N S_2} + H O = \underset{\text{Sinapoline.}}{C_7 H_6 N O} + \underset{\text{Bisulphide of carbon.}}{C S_2}$$

EIGHTH GROUP.

Alteration of Natural Alkaloids.

a. *Alteration of Narcotine by Oxidation.*

The excellent investigations of MM. Wöhler and Blyth on narcotine, which throw so much light on the most intimate constitution of that alkaloid, have brought to our knowledge new artificial organic bases, one of which, narcogenine, appears to form an integral constituent of narcotine.

On boiling a solution of narcotine in hydrochloric acid with bichloride of platinum, this latter loses some of its chlorine, which decomposes the water, and the resulting compounds are protochloride of platinum, 1 eq. of opianic acid, and 1 eq. of cotarnine.

Narcotine	$C_{46} H_{25} N O_{14}$	=	4 Pt Cl Protochloride of platinum.
Water	$H_2 O_2$		4 H Cl Hydrochloric acid.
Bichloride of platinum	4 Pt Cl_2		$C_{20} H_{10} O_{10}$ Opianic acid.
			$C_{26} H_{13} N O_6$ Cotarnine.

The two last substances may also be obtained on oxidising narcotine with a mixture of sulphuric acid and peroxide of manganese.

$$\underset{\text{Narcotine.}}{C_{46} H_{25} N O_{14}} + O_4 = \begin{cases} C_{20} H_{10} O_{10} .... \text{Opianic acid.} \\ C_{26} H_{13} N O_6 .... \text{Cotarnine.} \\ H_2 O_2 .... \text{Water.} \end{cases}$$

But during the oxidation of narcotine, there is also formed another base to which the name of narcogenine has been given. The following formula fully explains the nature of its formation:

$$2 \text{ eq. of narcogenine} = 2 (C_{36} H_{19} N O_{10}) = C_{72} H_{38} N_2 O_{20}$$

$$\underset{\text{Narcogenine.}}{C_{72} H_{38} N_2 O_{20}} = \begin{cases} C_{46} H_{25} N O_{14} .... \text{Narcotine.} \\ C_{26} H_{13} N O_6 .... \text{Cotarnine.} \end{cases}$$

Hence it follows that in its nascent condition, the cotarnine combines with the still undecomposed narcotine to form 2 eq. of narcogenine.

We may yet further regard the oxidation of the narcotine to take place as follows:

$$\underset{\text{Narcotine.}}{C_{46}\,H_{25}\,N\,O_{14}} + O_2 = \begin{cases} C_{36}\,H_{19}\,N\,O_{10} \;\ldots\; \text{Narcogenine.} \\ C_{10}\,H_5\;\;\;O_5 \;\ldots\; \text{Opianic acid.} \\ \;\;\;H\;\;\;O \;\ldots\; \text{Water.} \end{cases}$$

The formulæ adopted for narcotine and narcogenine are those of Dr. Blyth; those for cotarnine and opianic acid are the formulæ corrected by M. Gerhardt, to whom, conjointly with M. Laurent, we owe the possession of formulæ representing in equations the reactions we have described.

b. *Derivatives of Cinchonine by substitution.*

It has been shown by M. Laurent that on allowing chlorine and bromine to react on hydrochlorate of cinchonine we obtain certain new alkaloids; namely, chlorocinchonine and bromocinchonine, which are derived from the cinchonine by the substitution of chlorine and bromine in place of the hydrogen of that organic base.

Amongst the artificial alkaloids it yet remains to notice guanine, $C_{10}\,H_5\,N_5\,O_2$, which should almost be regarded as a natural alkaloid, since it is formed by processes occurring in nature, with which we are still unacquainted, and independently of the aid of chemical manipulations.

It probably arises from the decomposition of uric acid under the influence of reducing substances.

Such are the reactions by which the artificial alkaloids are produced: many of them, especially these last, present an altogether special character which forbids us to hope for many analogous instances; but those earlier described, admit of generalization, and the views regarding them may be extended to a large class of bodies.

We may entertain a hope that amongst the new alkaloids thus produced, especially if we conduct our researches on families characterised by the same number of atoms of carbon, we may discover bases identical with the natural alkaloids.

VIII.

MEMOIR.

ON THE INTIMATE CONNECTION EXISTING BETWEEN THE PSEUDO-VOLCANIC PHENOMENA OF ICELAND.

By R. Bunsen.

A careful study of the relations under which the innumerable systems of Thermal springs and *Fumeroles* are manifested in Iceland, must convince every attentive observer that an intimate connection exists between them and the active volcanoes of the island. The latter, upheaved on fissures, intersect the whole island in a parallel system of longitudinal lines, whose north-north-eastern extremity corresponds perfectly with the parallel expansion of the principal valleys and elevated ridges of the main system, and with the numerous volcanic fissures and dykes with which the country abounds; whilst the fumeroles and thermal systems appear to be likewise connected with this main direction. Following this line, independently of the course of the valleys and elevated ridges from which they proceed, they may often, as at Krisuvik or in the neighbourhood of Krafla and Leiznukr, be traced in lines passing transversely over mountains and valleys. This circumstance, and the common occurrence of solfataras, suffiones, thermal springs, and geysers, and still more the intimate connection existing between the phenomena of decomposition to which they give rise, lead, even on a superficial observation, to the conclusion that all these phenomena are merely to be regarded as modified expressions of one and the same fundamental cause.

In order to attain to a deeper insight into these intimately connected phenomena, it will, in the first place, be necessary to throw a glance on the hitherto imperfectly understood geognostic and hydrographic character of Iceland, and by these means to acquire a clear idea of the relations on which depends the remarkable development of the phenomena of the Icelandic springs.

The geological character of the volcanic system of Iceland is most strongly marked in the relations existing between the palagonite-mountain and the plutonic masses which have penetrated through it, and still continue to penetrate it during the eruption of volcanoes, still active, in the form of currents and strata of lava.

The palagonite-tuff* forms the most ancient member of this series of formations. Its formation immediately preceded the elevation of trachyte and of clinkstone, which last passes into the former, and both of which, owing to their relations of superposition and expansion, play a much less important part than is ascribed to them by Krug of Nidda in his *Treatise on Iceland.* The penetration of the older trap, a doleritic rock which is transformed into the most various kinds of amygdaloid, characterizes the third and most important period of elevation, during which this rock was upheaved in large veins, and frequently spread itself laterally in far extended strata through the tuffaceous masses. We may regard as appertaining to the fourth period, the olivine and basaltic elevations which have penetrated the trap formations in systems of veins of different ages, and which are especially manifested in the Island of Vidhey, in the Bay of Reykjaviker and on the Esja, as well as at innumerable other points of the northern and southern part of the island. The series of plutonic elevations closes with the fifth period of the older and more recent lavas.

The structural relations of the trap system which predominates over the whole island, exercise, in their relation to palagonite-tuff, the most marked influence on the hydrographic condition of the island. The general character of the stratification of this class of rocks is manifested by a tendency to assume a horizontal direction and a flattened superficies, independently of the innumerable elevations and dislocations occa-

* Named from Palagonia in Sicily.

sioned by local causes; so that the trap-strata on the declivities of the abruptly sloping valleys generally terminate in horizontal or gently inclining lines between the tuff-strata. This structure is most intimately connected with the general level of the country, which rises in a flat ascending arch, until it attains an elevation of 689 meters above the level of the sea, near the middle of the island, on the Sprengisandz, the point where the waters diverge to the north and south, This gently-rising elevated plateau, covered by innumerable moving glaciers, forms the basis of the grand ice-berg, called by the Icelanders, the Jökull, and which terminates similarly in a flat superficies, manifesting, with the exception of occasional sharp projections from its base, the structure in plutonic strata analogous to the above.

Inaccessible fields of snow cover the summits of the mountains, and reveal, at great distances, the limits of the region of glaciers, which penetrate with their huge masses of ice for a length of many miles, even to the lower range of the plateaux, and may be traced by the bluish reflection of their dazzling masses in the glacier ice. It is owing to these ice-bergs, which cover almost a tenth part of the island, that Iceland, taking into account its climatic relation, is characterized by so remarkable an abundance of atmospheric deposition, and it is to the same cause we must refer the singular development of the phenomena of springs, which is intimately connected with the peculiar structural relations of the palagonite rock. Vast masses of water break through the fissures and arches of the glaciers, or rush in cascades down the icy walls of the mountain-slopes, not unfrequently converting a district of many miles into a bottomless mass of moving mud, in which the streams accumulate before they can form for themselves a well-defined and regular bed for their waters. Innumerable inland seas, vast marshes and swamps, which make this barren and desolate country appear even more terrible to the eye of the traveller, are the consequence of such overflowings, diffusing a mass of waters over the elevated plateau of this island, which, finding its way into the deep declivities along the gently-inclining strata of rocks, serves to nourish the various systems of springs.

The dykes and fissures corresponding with this volcanic line of elevation must necessarily interrupt the course of these subterranean waters, and cause them to diverge into those deep ravines where a process of heating and evaporation must unavoidably be induced from the action of the heat of the volcanic soil. The water, elevated by the combined force of elastic vapour and hydrostatic pressure, then breaks forth in thermal springs, whose frequent north-eastern direction necessarily stands in the closest connection with the above-named general geognostic relations of the island. That it is from meteorological depositions that water is conveyed to the thermal springs, and a connection established, in consequence, between atmospheric and volcanic phenomena, is proved by the most undoubted facts. In the first place, nitrogen, which rises from the thermal springs, either pure or mixed with other gases, affords certain evidence of the atmospheric origin of these waters, since this gas, which cannot, by any possibility, be counted amongst the direct products of volcanic activity, has never yet been found, as far as can be ascertained by any approximative calculation, in a larger proportion to the mass of thermal waters than that corresponding with the solubility of the gases of the atmosphere in water. Another proof of the atmospheric origin of these springs is afforded by the small quantity of ammoniacal salts and organic extractive matters which are found to exist in the water, even where the latter is in further connection with the atmospheric air than that afforded by the narrow mouths of the springs. These observations do not, however, in any way exclude the possibility that the great quantity of water contained in the palagonite of the tuff-strata may take an active part in the development of gases by which the suffiones and geysers are characterized, and which, on occasion of the great eruptions of the volcanic islands of Iceland, force a passage for themselves through the craters in huge columns of ashes bearing the form of colossal pines.

A simple calculation shows that palagonite, whose density is 2·43, and whose combined water amounts to 17 per cent., should generate a quantity of vapour on being heated; which at 0° C. and Bar. $0{\cdot}^{m}76$ occupies 512·7 times the volume of the original rock, and which must necessarily find vent where the upheaved

fluid masses of lava come in contact with that rock at some great subterranean depth. The degree, however, in which these aqueous contents contribute to the formation of thermal springs involves points of consideration that are not included in the sphere of experimental investigations.

One of the most important questions associated with the Icelandic thermal springs has reference to the nature of their composition.

If it be true that the great atmospheric process of distillation gives rise to the flow of water to the springs, we may expect that their mineral constituents likewise admit of being explained by a reciprocal reaction of the originally pure water and of the gases dissolved in it on the rock constituting the base of the spring. Geology has, unfortunately, limited itself exclusively to hypothesis regarding this subject, or to the exposition of mere possibilities without investigating it experimentally with the circumstantiality it merits. Iceland presents the best field for such an inquiry in its remarkable thermal springs, and the innumerable geysers and suffiones which afford an exhibition of the most striking decompositions, and furnish us with a key for the experimental solution of many, I might almost say *all*, the questions which have hitherto been directed to these mysterious phenomena.

The Icelandic mineral springs, to which belong all the systems of geysers and suffiones, are distinguished from all others in Europe by the proportionally large quantity of silica which they contain; and if we except the acidulous springs which are confined to the western part of the island, the so-called beer-springs (*ölkilder*,) of the natives, we may divide the springs of Iceland into two main groups, according to their chemical properties, one of which would comprise the acid and the other the alkaline silica springs. The former belong to the actual solfataras, (the *Námar* of the Icelanders,) and owe their slight acid reaction more commonly to the presence of a small quantity of ammonia-alum or soda and potash-alum, than to their inconsiderable traces of free sulphuric or muriatic acids. They contain, besides, sulphates and chlorides of calcium, magnesium, sodium, potassium, and iron, also silica and sulphurous acid, or in the place of the latter, sulphuretted hydrogen

gas. They are especially characterized by depositions of gypsum and sulphur. Periodic springs of eruption are of very rare occurrence. The alkaline springs are the most prevalent, and constitute the periodic bubbling springs (geysers), as well as those designated in Iceland by the name of *Huer*, and which are generally warm, or even boiling. Their extremely slight alkaline reaction is owing to the presence of alkaline sulphides and the carbonates of soda and potash, which serve as solvents for the silica, and give rise to the silica-tuff formations by which these springs are so strongly characterized. Alkaline sulphates and hydro-chlorates are the salts most commonly found in these waters; they also generally exhibit traces of magnesia.

The process from which all these mineral waters derive their constituents is so much the more interesting from the detailed manner in which it may be traced. It appears in a series of very remarkable decompositions, experienced by the palagonite under the influence of the volcanic gases.

The following is the formula which I determined for this rock from experiments which have been given in detail in another Memoir*:

$$\left.\begin{matrix}\dot{M}g_3\\ \dot{C}a_{\ 3}\\ \dot{K}_{\ 3}\\ \dot{N}a_{\ 3}\end{matrix}\right\}\dddot{S}i_2+2\left\{\begin{matrix}\ddot{F}e\\ \ddot{A}l\end{matrix}\right\}\dddot{S}i+9\dot{H}.$$

* The experiments to which allusion is made yielded the following results:

		Oxygen.		Oxygen of the Isomorphous Bodies.	
Silica	37·417	.....	19·4280	..... 19·4280	4
Sesqui-oxide of iron	14·175	.....	4·2480	..... 9·4670	2
Alumina	11·165	.....	5·2190		
Lime	8·766	.....	2·4928		
Magnesia	6·036	.....	2·3382		
Potash	0·685	.....	0·1163	..... 5·1146	1
Soda	0·652	.....	0·1673		
Water	17·152	.....	15·2490	..... 15·2490	3
Insoluble residue	4·108				
	100·156				

If we assume that the oxygen of the isomorphous bases is as 4 : 2 : 1 : 3, and

The volcanic gases of Iceland, which act upon this rock and are acted upon by it, only differ from those of European volcanoes by containing a less considerable quantity of carbonic acid. They consist, as is generally the case, of sulphurous acid, sulphuretted hydrogen, carbonic acid, and hydro-chloric acid.

that of the whole amount 49·2586 of the oxygen, $\frac{1}{10}$ belongs to the lime and its isomorphous bases, $\frac{2}{10}$ to the alumina and sesqui-oxide of iron, $\frac{3}{10}$ to the water, and $\frac{4}{10}$ to the silica; and if, further, we divide the quantity of oxygen thus calculated among the separate isomorphous bases, making it proportional to the respective quantities of oxygen found, we shall obtain the following formula, which does not differ more considerably from the results of the experiment than might be expected from an isomorphous mixture.

Silica	37·947
Sesqui-oxide of iron	14·751
Alumina	11·619
Lime	8·442
Magnesia	5·813
Potash	0·659
Soda	0·628
Water	16·621
Residue	4·108
	100·588

This leads to the formula:

$$\left.\begin{matrix}\dot{Mg}_3\\ \dot{Ca}_3\\ \dot{K}_3\\ \dot{Na}_3\end{matrix}\right\} \dddot{Si}_2 + 2 \left\{\begin{matrix}\dddot{Fe}\\ \ddot{Al}\end{matrix}\right\} \dddot{Si} + H.$$

Palagonite approaches, therefore, very nearly to Oltrelite, which was examined by Damour, and of which the formula is—

$$\left.\begin{matrix}\dot{Mn}_3\\ \dot{F}_3\end{matrix}\right\} \dddot{Si}_2 + 2\ddot{Al}\,\dddot{Si} + 3\dot{H}.$$

Its place in a system, will, therefore, be next to that body. It only differs in its proportion of water from the formula of several of the Skapolitres investigated by E. Th. Wolf. The general formulæ of these three minerals are in very close relation to each other, as will be seen by what follows:

Skapolitre	$\dot{R}_3 \dddot{Si}_2 + 2R\,\dddot{Si}$.
Oltrelite	$\dot{R}_3 \dddot{Si}_2 + 2R\,\dddot{Si} + 3\dot{H}$.
Palagonite	$\dot{R}_3 \dddot{Si}_2 + 2R\,\dddot{Si} + 9\dot{H}$.

The latter, both here and at Etna, constitutes a far less important feature than at Vesuvius.

The chemical relations of nitrogen, ammonia, and their compounds, teach us with certainty, that although these substances are scarcely ever absent from volcanic exhalations; they are foreign to the actual force of plutonic activity. They undoubtedly belong originally to the atmosphere, or to organic nature, their occurrence being due to the water which holds them in solution and conveys them from the air to these subterranean depths.

The great abundance of the sublimations of muriate of ammonia observed in the neighbourhood of Vesuvius and Etna, serves rather to support, than to invalidate this view. It is further confirmed, in a very striking manner, by the phenomenon that occurred in the eruption of Hecla in 1846, when the lava current streamed forth from the deepest of the four newly formed craters, spreading itself over the plain of Thjorsa. In July, 1846, (only a few months subsequent to the eruption of the volcano) when I was sojourning in that district, the lower portion of the lava stream appeared studded over with smoking fumeroles, in which so large a quantity of beautifully crystallized muriate of ammonia was undergoing a process of sublimation, that, notwithstanding the incessant torrents of rain, hundreds of pounds of this valuable salt might have been collected. On surveying the stream from the summit of Hecla, it was easy to perceive that the formation of muriate of ammonia was limited to the zone, in which meadow lands were overflowed by the lava. Higher up, where even the last traces of a stunted cryptogamic vegetation disappear, the formation of this salt likewise ceased. The large fumeroles of the back of the crater, and even of the four new craters, yielded only sulphur, muriatic and sulphurous acids, without exhibiting the slightest trace of ammoniacal products. When we consider, that, according to Boussingault, an acre of meadow land contains so much as 32 pounds of nitrogen, corresponding to about 122 pounds of muriate of ammonia, we shall hardly be disposed to ascribe these nitrogenous products of sublimation in the lava-currents to any other circumstance than the vegetation which has been destroyed by the action of

fire. The frequent occurrence in Southern Italy of tuff decomposed by acid vapours containing muriate of ammonia, likewise confirms the hypothesis regarding the atmospheric origin of this salt. For the same body of air which can annually convey to a piece of meadow-land a quantity of ammonia corresponding to these large nitrogenous contents, must at least be capable of depositing an equal quantity of this alkali on tuff-beds saturated by acid water; which may be actually observed in some rare instances both in Southern Italy and Sicily.

Without entering more particularly into the question of the origin of the acid gases of volcanoes, the object of this treatise will be sufficiently attained, if we consider merely the remarkable phenomena of decomposition exhibited by the substance of palagonite under their action.

On treating pulverised palagonite with a large quantity of a solution of sulphurous acid, it is dissolved in the cold, and forms a fluid, coloured yellow-brown by salts of sesqui-oxide of iron. On heating it, the sesqui-oxide of iron yields its oxygen to the sulphurous acid. Sulphuric acid and protoxide of iron are produced in the proportion of one atom of the former to two atoms of the latter. The oxidation of sulphurous acid is likewise effected in part at the surface of the fumeroles, by the action of the atmosphere, or at the subterranean depths, by the atmospheric oxygen diffused in the spring-water. The sulphuric acid thus generated, is diffused among the constituents of the palagonite, which are liberated, together with a portion of silicic acid, and appear as sulphates in solution. This process represents the first stage of the fumerole action, which is manifested in the Námer or Solfatara of Krisuvik and Reykjatilid, on the grandest possible scale. Exhalations of sulphurous acid, sulphuretted hydrogen, sulphurous and aqueous vapours, here burst in the wildest confusion from the hot soil, consisting of palagonite-tuff, and spread themselves far over the steaming sulphurous fields, that are constantly in the act of being formed by the reciprocal decomposition of palagonite and this gas. The erupted gases and vapours assume the most different character on these plains, whose deceptive sulphurous and aluminous soil must be traversed with caution by the traveller who would avoid the danger of being drowned

in the hot mud. On the declivities of the mountains, where firmer trap, or lava rocks oppose an obstacle to their further advance, they burst foaming and hissing, in the form of vast columns of vapour, from the fissures and clefts of the rocks, giving rise to sounds like thunder when they strike the bottom over subterranean cavities. But where the spring-system inclines more towards the valleys and the loose tuff soils, the traveller continually meets with pools of boiling mud, in which a horrible bluish-black argillaceous paste rises in huge bubbles, which on bursting, often throw the boiling mud to a height of upwards of fifteen feet, accumulating its masses in crater-like ledges round the basin of the spring. These phenomena constitute a picture of the wildest devastation, only to be surpassed in horror by the dread waste of the dark rocky masses by which the scene is enclosed.

If the activity of the chemical decompositions witnessed in this remarkable theatre of volcanic activity, closed with the formation of sulphuric acid and the solution of palagonite, to which the latter gives rise, the relation existing among the earthy bases found in the acid siliceous springs would necessarily be the same as that existing in the constituents of palagonite itself; but experience shows that such is not the fact.

I here give the composition of a water, which I took, in August, 1846, from one of the largest boiling mud-cauldrons of

Composition of Water, in Ten Thousand Parts.

Sulphate of lime....	1·2712
Sulphate of magnesia	1·0662
Sulphate of oxide of ammonium	0·7333
Sulphate of alumina	0·3261
Sulphate of soda....	0·2674
Sulphate of potash	0·1363
Silica	0·4171
Alumina*	0·0537
Sulphuretted hydrogen	0 0820
Water	9995·6467
	10000·0000

* These salts are all regarded here as anhydrous; the free alumina, the small quantity of which brings it within the limits of the errors incidental to the experiment, may have been dissolved in excess by the alum of the water. The water contains, besides, a scarcely appreciable trace of protoxide of iron, muriatic acid and organic matter.

the Reykjahlider solfatera, between the north-eastern declivity of the Nàmarfjall and the Burfell lava stream.

If we reckon the bases of the salts, which scarcely amount to $\frac{1}{400}$ part of the water*, as 100, and compare the preceding numbers with the relation of the bases in palagonite, we shall discover a great difference.

Relation of Bases.

	In Palagonite†.	In the Water of the Suffiones.
Oxide of iron	36·75	0·00
Alumina	25·50	12·27
Lime	20·25	42 52
Magnesia	11·39	29·42
Soda	3·44	9·51
Potash	2·67	5·98
	100·00	100·00

A glance at this composition will suffice to show, that the sulphate of iron, produced by the action of the sulphurous acid on palagonite, does not occur in the water; that the alumina of the water exists in a much smaller relation than that which corresponds with the composition of palagonite; that the gypsum stands in a less considerable relation to the remaining bases of the water than is required by the composition of palagonite; and, finally, that the relation of the magnesia, soda, and potash, taking into account the errors incidental to the experiment and the oscillations to which these bases are subject as isomorphous bodies, perfectly express the relation of these constituents in palagonite.

These facts prove, in the most decided manner, that the activity of the chemical decompositions induced by the sulphurous acid does not end in the solution of palagonite. It still remains to determine how this activity is manifested in a series of actions by which the quantity of protoxide of iron formed, together with a portion of the alumina and lime, are again removed from the solution. The separation of these constituents depends on a very remarkable relation of the sub-

* We may thus see how inexact and exaggerated are the data yielded, even by the most recent travellers, of the composition of these fumerole waters. These waters have so little taste that they might, in case of necessity, be used for drinking after they had been cooled and filtered.

† Liebig's *Annals*, bd. lxi. H 3, s. 273.

stance of palagonite, which indicates a mode of origin of many many of the older rocks that has hitherto remained wholly unheeded, and which may throw a new light on some metamorphic structures, whose origin must otherwise be considered to belong to the most mysterious problems of geology.

One might indeed be inclined to ascribe the total absence of oxide of iron in the natural solutions of palagonite to its precipitation by the free or carbonated alkalies which, under special circumstances, proceed, as I am about to show, from the decomposition of this mineral; but an explanation of this nature appears wholly inadmissible, as the alumina must have been precipitated by alkalies before the protoxide of iron, or *simultaneously with* it; facts that are alike incompatible with the presence of this substance in most suffione waters. The true cause of the phenomenon is different. Thus I have found that palagonite possesses the property, on being digested in a neutral solution of sulphate of iron, of precipitating the protoxide of iron, as a hydrate or rather as a silicate, with the formation of sulphate of lime. Free sulphurous acid, therefore, originally dissolves the oxide of iron of the tuff as a proto-salt, together with a portion of its remaining constituents; but when the solutions have been neutralised by their passage through the rock, the oxide of iron is again deposited as hydrated protoxide, on being brought further in contact with the rock, or as hydrated sesquioxide when oxygen is present. The decomposed palagonite is thus converted into alternate and irregularly penetrating beds of white ferruginous and of coloured ferruginous fumerole clay. The limits of these deposits indicate the strata where the first action of acid solutions has passed into the second one of neutral solutions. The solfataras of Krisuvik and Reykjahlid are rich in instructive examples of this nature. Thus, for instance, we observe on the north-eastern wall of the Námarfjall at Reykjahlid in the neighbourhood of the largest of the cauldrons of boiling mud, a small ravine, formed by the offshot of the waters and by the jets of steam issuing from the fumeroles, in which these depositions are disclosed to a considerable depth, exhibiting in the clearest manner the phenomenon of alternating colours. One is astonished at observing the great similarity existing between the external phenomena of

these metamorphic depositions of clay still in the act of formation, and certain structures of the keuper formation.

Thousands of years hence, the geologist, who explores these regions, when the last traces of the now active fumeroles have vanished, and the clay formations have become consolidated into marl-like rocks by the silica with which they are saturated, may suppose, from the differently stratified petrographic and chemical character of these strata, that he was looking at floetz strata formed by deposition from water, as in the case of many structures of the secondary period. Notwithstanding that this metamorphosed rock originally consisted of a homogeneous mass of palagonite, the alternating composition of whose interior is owing to a secondary transport of its constituents.

The same action which is exercised by palagonite on the neutral solutions of sulphate of protoxide of iron occurs also in the sulphates of alumina and sesqui-oxide of iron. Both of these bases owe to this their precipitation from neutral solutions, with the formation of gypsum; so that not only is the alumina removed from the suffione waters, but it is transported from one part to another within the domain of these decompositions. A great variety and inequality must consequently be induced in the composition of the argillaceous strata, affected as it is by the incessant changes in the place of eruption of gases, by the special relations of water-currents, and by the saturations going on in the interior of the rock.

We see from these considerations, that sulphate of lime is a main product of these reactions, appearing in the second as well as the first stage of the decomposition of the palagonite. Palagonite exercises no further influence upon this or any other of the soluble products of decomposition. The inconsiderable solubility of this salt combined with its great capacity for crystallization gives rise to its constant separation under very remarkable relations.

The clay of the fumeroles becomes filled up with depositions of this substance. At the surface, especially, where the deposition is favoured by slow evaporation, innumerable crystals of gypsum, often an inch in diameter, may frequently be observed loosely surrounded by the argillaceous mass, as at the

solfataras on the Leirnukr. These crystals being very pure, but not apparently very fully developed.

At the mountain ledge of the Námarfyall and at Krísuvik, this gypsum is found to penetrate the argillaceous masses in *connected strata* and *floor-like depositions*, which not unfrequently project as small rocks where the loose soil has been carried away by the action of the water. These depositions are sometimes sparry, corresponding in their exterior very perfectly with the strata of gypsum so frequently met with in the marl and clay formations of the trias.

Their deposition is owing to a fact that has not hitherto been sufficiently regarded in the explanation of geological phenomena, viz.: that substances crystallizing from solutions are more readily deposited on a surface identical with their own (although at a considerable distance from the limits of their solubility), than on substances different from themselves. These depositions of gypsum increase, therefore, in these formations in the same manner as we observe small crystals to enlarge in a solution, without any deposit being formed on the sides of the vessel; much salt being removed from the solution (not by a change of temperature, but owing to the cohesive force emanating from the crystal,) so that no further deposit can be made on the particles of bodies of a different nature. The process of crystallization here comes within the domain of mechanical forces, since it causes, by the expansive growth of the layers of gypsum, the upheaval of the moistened clay deposit, or compresses it towards the exterior as the first-named masses increase in quantity*.

* The attention of geologists has hitherto been almost exclusively directed to the metamorphism of rocks from the action of fire. The metamorphic transformations effected by the action of gas and water at low temperatures, as we still see them exemplified on a small scale in the fumeroles, must, however, have played a no less important part in the more ancient plutonic disturbances, and exercised an immeasurable degree of influence in the formation of the substance, constituting the accumulated masses of the strata of the secondary period. I have endeavoured, in the present treatise, to bring prominently forward some indications and relations that may, perhaps, lead the geologist in the right path for investigating these structures. Everything seems to indicate that we are justified not merely from observations, but more from experimental investigations, in referring the metamorphoses of rocks to hydatothermic and

On a more attentive consideration of these phenomena, we can scarcely avoid the conviction that the origin of a portion of the vast deposits of gypsum, which so frequently characterise the marly-argillaceous strata of the later flœtz series, and in which the total absence of calcareous conchylia points to the action of acid vapours, is due to a chemically-identical, but perhaps geologically-different, action. A careful investigation of the varying composition of these marly deposits, having special reference to their mutual relations to one another and to the strata containing oxide of iron and deposits of gypsum, would, therefore, prove of the greatest interest in studying the history of such flœtz-beds. I propose, on a future occasion, to enter more fully into the relations of the tertiary clay formations to basaltic, doleritic, and trachytic tuff, since these fumerole actions throw great light on the subject.

Before I quit the phenomena of springs and turn to those embraced by the alkaline waters and the geyser-formations to which they give rise, I must not omit to notice some few products which, although less prevalent, nevertheless belong to the characteristic phenomena manifested by the activity of the solfataras in Iceland. Among these, I reckon plumose alum, iron pyrites, sulphide of copper, sulphate of copper, and, as the most important of all, sulphur itself. The formation of plumose alum is limited to the surface of the fumerole clay, such soluble salts being only found at periods when a dry atmosphere favours their efflorescence on the ground. Such depositions do not depend on a spontaneous evaporation alone of the suffione water, which is so poor in alumina, or even on the evaporation induced by the heat of the volcanic soil, but must rather be referred to the sulphurous gases that penetrate through the hot soil; and they usually indicate the portion of the smoking mud-crust which the traveller must tread with extreme caution, in order to avoid the danger of being burnt. It may be

pyrocaustic—or where these occupy the same scene of action—to hydatocaustic formations. I do not know, however, whether the time has yet arrived when we may introduce these denominations into the nomenclature of science. Such distinctive appellations certainly remain devoid of application until the test of experiment has decided the question in all its bearings. And geological chemistry is, unfortunately, still far from having attained to this object.

plainly seen that the remarkable property possessed by palagonite to precipitate neutral solutions of alumina, must limit the formation of alum to those localities where a constant flow of acid, more particularly sulphurous acid, is kept up by the action of the fumeroles. Sulphuretted hydrogen gas, which accompanies the gaseous exhalations of these suffiones, experiences, where in contact with the porous fumerole clay, the same kind of contact combustion which has lately been so ably described by Dumas, at the expense of the oxygen of the atmosphere; and of which the principal product is sulphuric acid. Every fall of rain which dissolves the salt and carries it to the inner strata of the palagonite, not only withdraws it, but actually gives rise to a second process of decomposition within the rock, in which the alumina is precipitated by the palagonite, which, in its turn, passes through all the different phases of decomposition that, as I have already remarked, begin by the neutralization of the solution and terminate in the precipitation of the alumina and the oxide of iron. Hence it follows, that the phenomena of the alum formations which, in dry weather, run through their whole course in the space of a few days, and as rapidly disappear in rain and a humid state of the atmosphere, bear no relation to the small quantity of alumina contained in the water of the suffiones.

The main attendant of the suffiones, and the one by which they are actually converted into solfataras, is sulphur, which is found deposited in very large quantities on the Námar of Krísuvik, of which we have already frequently spoken; and to a still more considerable extent in the neighbourhood of the Krafla. It appears to be essentially due to the reciprocal reaction of sulphurous acid and sulphuretted hydrogen gas. At all events, these gases which, as is well known, mutually decompose each other, depositing sulphur, constantly accompany sulphur sublimations, exhibiting mutually antagonistic conditions. It must be admitted that I have endeavoured unsuccessfully to detect by the most sensitive test paper the presence of sulphuretted hydrogen in the fumeroles of the four recent craters of Hecla, which are so rich in sulphurous acid and sulphur. I was equally unsuccessful in discovering traces of

sulphuretted hydrogen gas by the use of the same means, when I investigated the gas that streamed from the fissures and crevices of the innermost and highest of the craters of Hecla, which have been upheaved during the late eruption. The investigation was rendered peculiarly difficult from the column of gas that issued from the uppermost and innermost walls of the crater. A phenomenon may, however, be noticed in the immediate effects of the eruption, which indicates the presence of some inconsiderable traces of this gas, which has escaped undecomposed with the great excess of the liberated sulphurous acid.

On bringing a lighted cigar near the evolving gas the well-known phenomenon of contact-combustion is at once manifested, which was first observed at the fumeroles of the solfataras of Naples, and may be considered as exercising the most sensitive reaction on sulphuretted hydrogen gas*. A dense cloud of vapour is instantaneously observed to emanate from the burning body, diffusing itself far over the ravine and the plain of the fumeroles. This phenomenon could be called forth at Hecla even where there was no smell of sulphurous acid, and where paper, saturated in acetate of lead, exhibited no trace of sulphuretted hydrogen after having been exposed for many hours to the action of the vapours. It is, moreover, a very common occurrence in Iceland to find that the water of the boiling cauldrons, although giving indications of sulphurous acid only, is permeated by gases impregnated by a large quantity of sulphuretted hydrogen—a circumstance which proves that the last gas is decomposed on its solution in the fluid containing sulphurous acid, and that this decomposition is accompanied by the deposition of sulphur. Where these gases appear in contact with aqueous vapour, thick crystalline crusts of sulphur may be observed deposited round the mouths and over the top of the fumeroles.

* Almost all the hot springs and fumeroles of Iceland exhibit this phenomenon. Even the light vapour which rises from the clear bluish-green water of the basin of the large crater is converted, on the approximation of a burning body, into a dense cloud of vapour, which envelopes the whole mirror of the water and spreads itself in all directions, from the point of contact, as if from a centre of combustion.

Their deposition is apparently owing to a mechanical transportation of the flowers of sulphur by the vapour escaping, and this formation may not inaptly be compared to the depositions of dust and soot, which, when finely disintegrated, are mechanically borne to great distances by the currents of the atmosphere.

Another and far less considerable part of the sulphur is deposited in the form of a delicate white powder, by which the argillaceous strata seem not unfrequently to be cemented in a manner. This deposition appears to be owing to the decomposition of the sulphuretted hydrogen by atmospheric oxygen, or it may also depend on vapour of sulphur that accompanies the stream of aqueous vapour. This latter kind of sulphurous deposition can be exhibited by a very simple experiment, for when water containing flowers of sulphur is boiled, a considerable quantity of this body may be observed to pass into the receiver in the form of a delicate white powder. I have only found sulphur in a state of fusion in the two largest of the recent craters of Hecla, the *upper* walls of which manifested, at different parts of their superficies, a temperature far exceeding 100° C., this being especially the case in the vicinity of the many fissures that run in a north-eastern direction parallel with the back of the crater. The observation was made in July 1846, and, consequently, some months after the last great eruption.

Another product of fumerole activity deserving, in a high degree, the attention of geologists, is iron pyrites, which very frequently fills up different portions of the clay deposits produced by the decomposition of palagonite, appearing in the form of small crystals, often very beautifully developed. Its formative process, which can be most plainly observed, throws considerable light on the formation of the iron pyrites, which occurs so frequently in the older argillaceous marl beds, especially in the trias, for although the two processes may originate in very different geological conditions, there can be no doubt that they are of the same chemical nature.

These formations really depend upon a very remarkable decomposition experienced by the substance of the palagonite under the action of sulphuretted hydrogen. In consequence

of this, proto-sulphide of iron and alkaline metallic sulphides are produced. The palagonite is converted by the former into a black mass, which occasionally imparts a bluish-black colour to the clay of the boiling mud-pools, and is not unfrequently manifested in the spring by the deposition of a sandy-black powder. The alkaline metallic sulphides, on the contrary, are dissolved by the boiling water, and converted, wherever they come in contact with sulphur, into poly-sulphides. No one who is familiar with analytic investigations can be ignorant of the facility with which these bodies dissolve slight traces of proto-sulphide of iron with a green tint, and then again are able to deposit it under peculiar circumstances. It will, therefore, be easily understood how the higher oxide of iron, converted into proto-sulphide of iron, by sulphuretted hydrogen, with the separation of sulphur, should be dissolved by the simultaneously formed alkaline poly-sulphides; and abstracting from the latter an atom of sulphur should again be precipitated in crystals of bisulphide of iron, or iron pyrites. The mode in which the iron pyrites is formed fully confirms this view. The coloration by oxide of iron stands in an inverse ratio to the quantity of the crystals formed, the former increasing in depth as the latter diminish in quantity, the pyrites being only found in its greatest possible development where the oxide of the iron had wholly vanished from the clay.

I shall postpone for another occasion the consideration of the conclusions which might be drawn from these processes regarding the origin of the older clay-formations. It is easy to perceive that these pyrites-formations have nothing in common with those that have been produced by the decomposition of sulphates by the action of organic matter, since they occur as well in the highest crater of Mount Hecla, where all idea of the co-operation of organic substances must fall to the ground, as in the geysers of Reykir and in the solfataras of Krísuvik and Reykjahlid.

I must not omit to mention, that some compounds of copper, arising from secondary actions, likewise appear as separate products of fumerole activity, as, for instance, sulphide of copper, krisuvigite, and sulphate of copper. The formation of these

substances is, however, too simple to require any separate notice; although we would observe that the diffusion of copper in the great Icelandic volcanic system seems to receive some elucidation from the occurrence of pure copper in the trap formations of the island of Faroe.

On considering the numerous chemical processes, whose foci are the solfataras and fumeroles of Iceland, we cannot fail to see that it is the great abundance of volcanic gases, especially sulphurous acid, which, together with the reaction of palagonite, constitute the main character of these phenomena. Where these gases are no longer prominently manifested, or where sulphurous acid is almost wholly absent, the scene suddenly changes. The observer finds himself at once transported to a totally different field of pseudo-volcanic phenomena, as it is represented by the innumerable thermal and geyser systems. The connection existing among these phenomena and those we have been considering, is not less simple than it is easy of comprehension. Here, too, the relation of the palagonite substance to the composition of the waters of the springs constitutes the starting point, from whence the observer, aided by experiments, may advance, step by step, from the most inconsiderably manifested chemical actions, till he arrives at a knowledge of that wonderful mechanism by which the grand activity of the violent sources of eruption in Iceland is maintained. As it will be necessary to direct our attention to some definite locality, I would select the Great Geyser, as the best known of all the intermitting eruptive springs of Iceland.

The thermal group belonging to this celebrated spring lies on the outskirts of the great glacier plain which constitutes the elevated plateau in the centre of the island, almost exactly south-west of the highest point of Hecla, and only distant from it about 20 geographical miles in a direct line. The height of the geysers over Reykjavik (at the residence of Counsellor of Justice, Thorstensan,) amounted, according to the barometrical measures made on two consecutive days, to 112·8 met. and 107·2 met. Their main direction runs about N. 17° E. and is therefore almost parallel with the chain of Hecla and with the general direction of the fissures. The oldest rock forming the base of the springs is also here com-

posed of palagonite tuff, penetrated lengthwise by a vein of clinkstone, running from the western margin of the springs. Here and there a few boiling and vapour springs burst from the clinkstone, at a height of about 55 met. above the Great Geyser. The main focus of thermal activity is, however, situated in a loose palagonite tuff at the foot of the opening in the clinkstone. This rock, on the north-western side of the geyser-cone, where the strata are broken through by a jet of water, is covered above by the siliceous deposits from the spring, whilst below it becomes transformed into the variegated fumerole clay, of which we have already spoken as a product of the decomposition of palagonite.

The characteristic phenomena of decomposition which mark the acid siliceous waters, are never wholly absent from the class of alkaline springs. Here, too, where the fumerole clay is freed from siliceous incrustations, a foaming pool may occasionally be met with, the dark viscid mud of which rises in huge bubbles, or a steaming bed covered with crystals of gypsum and alum, or, finally, a deposit of sulphur superposed on the clay, or even on the siliceous incrustations. But these phenomena, which depend on the occurrence of small quantities of sulphurous acid, sink into insignificance, or I might almost say, entirely vanish before the stupendous phenomena developed by the action of carbonic acid, sulphuretted hydrogen, and heated water, on the substance of the palagonite. In the mutual reaction of these four substances are combined all the conditions required by nature to convert, in the course of centuries, simple boiling springs into geysers, whose clear, vapoury, and foaming columns of waters, shall burst from the summits of their self-created siliceous tuff-craters, either continuously, or at periods extending from a few minutes to hours, or days. These geysers and the other alkaline siliceous springs of Iceland, do not evince that dreary character of wild devastation which is manifested by the fumeroles and solfataras, with their boiling mud-pools and their steaming fields of sulphur. The eye rests rather with pleasure on the white ledges and stalactites, which rise now in the form of small conical craters, then in long furrows and vast basins, and again in round openings of the most regular configuration.

It will be necessary here to pause a few moments for the consideration of these incrustations. Their structure is simple and easy of explanation. It will be seen from the composition of the water of the geysers, as given in a subsequent part of this paper, that the silica is dissolved in the water by alkaline carbonates and in the form of a hydrate. No trace of silica is precipitated on the cooling of the water, and it is only after the evaporation of the latter that silica is deposited in the form of a thin film on the moistened sides of the vessel where evaporation to dryness takes place, whilst the fluid itself is not rendered turbid by hydrated silica until the process of concentration is far advanced. This apparently trivial circumstance is of the greatest importance in the formation of the geysers. It will be evident that the basin of the spring, in which the constantly renewed water affords only a very small field for the process of evaporation, must remain free from siliceous formations, whilst the margins projecting beyond the level of the water, will readily become covered by a siliceous incrustation owing to the rapid and easy drying of the moisture attracted by a capillary force. Further on, where the water spreads itself over the surface surrounding the spring, the incrustations increase in proportion as the surface of evaporation expands. As the basin of the spring has no part in this incrustation, it becomes converted into a deep tube as it is gradually enclosed by a hillock of siliceous tuff, combining, when it has reached a certain height, all the requirements necessary to convert it into a geyser. If such a tube be narrow and be filled with tolerable rapidity by a column of water strongly heated from below by the volcanic soil, a continuous geyser must necessarily be produced, as we find them in so many parts of Iceland. For it will easily be understood that a spring, which originally did not possess a higher temperature at its mouth than that which would correspond to the pressure of the atmosphere, may easily, when it has been surmounted by a tube, formed by gradual incrustation, attain at its base a temperature of upwards of 100° C, owing to the pressure of the fluid resting in the tube. The mass of water rising in such a spring, which is constantly renewed from below, and possessing in the natural shaft of the spring a temperature of 100°, must imme-

diately, on its escape from the mouth of the tube, experience a diminution of temperature corresponding to the diminished pressure of the atmosphere, by which the whole excess of heat above 100° will be expended in the formation of vapour. The water raised by the expansive force of these vapours, and mixed in a white foam, forces itself from the mouth of the spring foaming and hissing in one continuous gush. Iceland abounds in springs of this kind; although the Reykholter valley presents, perhaps, the largest number to be found in any one spot. I shall not, however, enter into any more circumstantial description of them, since the subject is only one of secondary interest. When the geyser tube, formed by the process of incrustation, is sufficiently wide to afford a considerable degree of cooling to the water at its surface, and the jet which is heated upwards of 100° C., falls but slowly back to the base of the wide funnel, we find all the requirements necessary for converting the spring into a periodically recurring geyser, which bursts suddenly forth by the action of the developed force of the vapour, and then forthwith falls back to a state of long continued repose. The Great Geyser is the most remarkable of these springs, which have been regarded as natural accumulators of the force of vapour.

Immediately after an eruption, the water which fills the tube to the height of 1 or 2 met., gradually rises during several hours to the margin of the basin, whence it flows over the cone in the form of a small cascade.

It may easily be shown by experiment, that the column of fluid filling the tube, is constantly being heated by water entering it from below, whilst it experiences a constant cooling and evaporation above on the broad surface of the basin. Evaporation is likewise effected within the funnel itself by means of a current which rises and falls in its upper portion; driving a column of heated water up the centre of the funnel, it spreads itself over the surface of the basin towards the edges, and after the evaporation has been completed flows back to the funnel.

The direction of this current may be observed by throwing a few shreds of paper into the middle of the basin of the geyser, as they will be driven to the margin of the upper

surface, and then again be carried back to the bottom of the tube.

The changes of temperature experienced by the different strata of the column of water when subjected to the alternately cooling and heating influence during the time intervening between the eruptions, have been made the subject of a series of thermometrical measurements, conducted conjointly by M. Descloizeaux and myself at the Great Geyser. The following is a portion of the results obtained*:—

Height from the Bottom.	Temperature.
6th of July. 8h 20m P. M.	
0·3 met.	123°·6 C.
4·8 „	122°·7 „
9·6 „	113°·0 „
14·4 „	85°·8 „
19·2 „	82°·6 „
7th of July. 2h 55m P. M.	
0·3 „	127°·5 „
5·0 „	123°·0 „
9·85 „	120°·4 „
14·75 „	106°·4 „
19·55 „	85°·2 „
7th of July. 7h 58m P. M.	
0·3 „	126°·5 „
5·0 „	
9·85 „	121°·8 „
14·75 „	110°·0 „
19·55 „	84°·7 „

From these results it follows:

1. That the temperature of the column of the geyser decreases from below upwards, as had already been shewn by Lottin and Robert.

2. That, setting aside small disturbances, the temperature goes on increasing regularly at all points of the column from the time of the last eruption.

3. That the temperature in the unmoved column of water

* A full report of these observations is given by M. Descloizeaux, in the *Annales de Chim. et de Phys.*, 3 série, t. xix.

did not, at any period of time up to a few minutes before the great eruption, reach the boiling-point that corresponds to the atmospheric and aqueous pressure at the point of observation.

4. That it is at mid-height in the funnel of the geyser where the temperature approaches nearest to the boiling-point corresponding to the pressure of the column of water, and that it approaches nearer to this point in proportion to the approximation of the period of a great eruption.

The curves of Plate II., fig. 1, are a graphical exhibition of these relations. Curve 1 represents the temperatures at which the column of water would be brought into a state of ebullition throughout its whole length, the irregular lines 2, 3, and 4, the temperatures observed of the column of water at the respective periods of 10 minutes, of 5 hours, 31 minutes, and of 23 hours, 13 minutes, before a great eruption.

If we now consider the period which immediately precedes an eruption, we shall find that only a very slight impulse is necessary to bring a large portion of the column of water suddenly into a state of ebullition, and, as we shall soon see, even to produce an eruption. Every cause that tends to raise this column of water only a few meters, must necessarily be attended by this result. If, for instance, we assume this elevation to be equal to 2^m, the column of fluid pressing on the point *a* (fig. 2) will be shortened by the height *a b*. The temperature *a* of the stratum of water lying under a pressure diminished by *a b* is now about *b c*, or 1° higher than the corresponding boiling-point of the water. This excess of 1° is immediately expended in the formation of vapour, generating in the present case, as may be proved by an easy calculation, a stratum of vapour nearly equally high with the stratum of water 1^m in height. By this diminution in the superincumbent water a new and deeper portion of the column of water is raised above the boiling-point; a new formation of vapour then takes place, which again occasions a shortening in the pressing liquid strata, and so on, until the boiling has descended from the middle to near the bottom of the funnel of the geyser, provided always that no other circumstances have more speedily put an end to this process.

It appears from these considerations that the column of

water in the funnel of the geyser extending to a certain distance below the middle, is suddenly brought into a state of ebullition, and further, as may be shown by an easy method of computation, that the mechanical force developed by this suddenly established process of vaporization is more than sufficient to raise the huge mass of the waters of the geyser to that astounding elevation which imparts so grand and imposing a character to these beautiful phenomena of eruption. The amount of this force may easily be ascertained by calculating from the temperatures of the preceding experiments, and the known latent and specific heat of the aqueous vapour, the height of the column of vapour, which would be developed by the ascent to the mouth of the geyser of a section of the column of water. If we designate the height of such a column of water in the funnel of the geyser by h; its mean temperature expressed in centesimal degrees by t; the latent heat of the aqueous vapour by w; the density of the latter compared with that of the water by s; and the co-efficient of expansion of the vapour by d; we shall find that the excess of heat of the water above the boiling-point under the pressure of one atmosphere is $t-100$. But the height, h, of the section of the column of water, which at the mouth of the geyser, that is to say, under the pressure of one atmosphere, would be converted into vapour by the quantity of heat, $t-100$, would be to the whole height of the water column, h, as $(t-100):w$. A column of water of the height $\frac{h\,(t-100)}{w}$ would therefore be evaporated at the mean temperature t, if the water were under the pressure of one atmosphere. Hence, it directly follows that the height, H, of the column of vapour sought at 100° and 0^m 76, will be

$$\mathrm{H} = \frac{h\,(t-100)\,(1+100\,d)}{w\,s}.$$

On applying this formula to the value of the numbers found by observation, we obtain the remarkable result that, in the period of time immediately preceding an eruption, a column of water only 12^m in length, which projects from 5^m to 17^m above the base of the tube, generates, for the diagonal section of the geyser, a column of vapour 638^m 8 in height (assumed

to be at 100°, and under the pressure of one atmosphere). This column being developed continuously from the upheaved mass of water, as the lower strata reach the mouth of the geyser. The whole column of the geyser, reckoned from the point where its temperature amounts to 100° C. down to the base, is capable, according to a calculation of this kind, of generating a similar column of vapour, 1041^{m} in height*. We can easily understand the reason that this enormous force should not be expended in one single jet of eruption, when we remember that the jets of water erupted in the air are continually falling back into the tube of the geyser, and interrupting, at different moments, the force of the upheaving column of vapour, which is condensed in the cooled water as it falls, until the temperature of the latter again reaches the boiling-point, and has consequently regained the power of being again propelled upwards. At the same time the water may be seen flowing from the basin back into the funnel, between the different separate ascents of the water. Occasionally, the water even appears as if it were forcibly drawn back.

The condensation in question, with the consequent restoration of heat to the water of the geyser, explains, at the same time, the fact of the great eruptions continuing frequently for a period of more than five minutes.

We now see the causes to which the column of water owes the slight elevation which imparts the first impulse to the eruption. The greater portion of the Icelandic thermal springs exhibit the peculiar but easily explained property of giving rise periodically, at certain points in the water of the thermal basins, to a number of large bubbles of vapour, which become suddenly condensed on rising into an upper and cooler stratum. This invariably occasions a slight detonation, accompanied by a hemispherical elevation, and an instantaneously succeeding depression of the surface of the water. Even the Great Geyser is characterised by a periodic succession of these detonations

* I have assumed, for the sake of greater simplicity, that the temperature of the water in the tube of the geyser does not increase in a uniform curve, but in broken lines. On the first assumption the calculation would, of course, yield a somewhat higher column of vapour.

of vapour, beginning about four or five hours after a great eruption, and continuing, at intervals of from one to two hours, until the next eruption; immediately preceding which they occur in rapid succession and extreme violence. The cause of the periodicity of these detonations admits of an easy explanation; for it will be readily understood that when a stratum of water under the continuous influence of the heat of the volcanic soil, is brought into ebullition in the conducting channels of the tube of the geyser, and the vapour formed by its ascent into the higher and cooler masses of water is again condensed, the temperature of this boiling stratum is so far lowered by the formation of vapour, that it requires some length of time before it can be heated again to the boiling-point after the condensation of the vapours that have ascended in the water. The periodic elevation of the masses of water effected in the geyser by these means appears rarely to exceed 1 or 2 metres, if we may judge by the average height of the mass of water which is forced from the mouth of the tube in the form of a conical elevation. A glance at the graphic representation given in fig. 2 will, however, show that such an upheaval as this is insufficient to raise any stratum of water to an elevation where it could be brought to a state of ebullition, (in consequence of the diminution of pressure existing there,) until the mass of water would, by gradual heating, be brought to the temperature of the broken line, 2; and such is actually observed to be the case a few minutes before an eruption. All the other upheavals preceding this period would only be able to drive partially the lower heated masses of water by a sudden impulse into the upper part of the tube of the geyser, where these masses are brought into a state of ebullition, owing to the diminution of the pressure. These smaller eruptions may, therefore, be regarded as abortive beginnings of the larger, being unable, to propagate themselves beyond a short distance from the point of origin of the vapour, from the low temperature of the column of water.

On considering all the phenomena presented by the eruptions of the geysers, we cannot for a moment doubt that the main seat of the mechanical force, by which the mass of water is thrown up and converted into boiling foam, is actually

situated in the funnel of the geyser. This view is very beautifully confirmed by observing the manner in which the water is set into motion during an eruption.

In order to obtain a clear knowledge of these internal processes, I have frequently sunk stones weighing several hundred grammes, and marked by different bands, suspending them by thin threads at different depths in the geyser funnels filled with water. The only stones that were thrown from the spring to heights of upwards of 100 feet proved to be those suspended near the surface, whilst those that had been sunk to greater depths never exhibited themselves. Stones weighing many kilogrammes, placed between the basin of the geyser were, however, carried back into the tube of the geyser with the mass of water returning from the basin in the intervals between the separate jets, and these were again erupted. This fact, which may appear strange at first sight, is in perfect harmony with the formation of the jets of eruption within the tube. The mixture of vapour and water, of which these spouts or jets consist, must necessarily move with constantly increasing rapidity as the expansion and development of the vapour increase at the mouth of the geyser, so that the moving fluid may thus be able to carry with it, near the mouth of the basin, heavy objects which it would be unable to upheave at any greater depths. Such experiments clearly show, that we must regard the tube of the spring as the actual focus of the mechanical forces that maintain the action of these periodical eruptions, and further, that whatever communication may exist by means of lateral channels between this main thermal stratum and the heated masses of water within the ground, the water must still be able to develope considerable masses of vapour and convey them to the apparatus of eruption, owing to the diminution of pressure consequent on this phenomenon. A necessary result of these circumstances is, that the eruptions gain in force, in proportion as they lose in regularity of their intermission and duration. The co-operation of this secondary development of vapour is shown by the remarkable fact, that the spouts of water move in a rotatory direction during great eruptions; a phenomenon that can only be explained by a lateral influx of vapour. The rotatory motion cannot certainly

be observed through the dense clouds of vapour that envelop the erupted masses of water, but I accidentally discovered it in an experiment originally instituted with a view of measuring the pressure at the base of the geyser column during a great eruption, by means of a small maximum manometer*, which was suspended by a line in the middle of the spring, and sunk very nearly to the bottom. A number of stones, which I sunk suspended to fine threads, that were secured at various parts of the circumference of the funnel, separated from the threads without being again erupted, however, with the water. The threads themselves, which were suspended round the circumference of the tube of the geyser, and parallel with the line at a distance of 1·5 metres, were whirled into an inextricable coil round the line of the manometer, which could only arise from a gyratory motion in the column of water. This also is undoubtedly the cause of that tangential expansion of the water-spouts, by which they are frequently spread far beyond the margin of the tuff-basin, imparting a form to the eruption somewhat similar to the species of fire-work termed a *bouquet de feu.*

On considering the conditions of the activity of these eruptive springs, we shall scarcely be led to expect any special regularity in the magnitude, duration, and succession of the eruptions and the detonations of vapour†. The supply of water to the springs, which varies with the state of weather, and the evaporation at the surface, which depends on the temperature and intensity of the currents of air, must both be most intimately associated with the changing play of these phenomena‡. If the activity of the eruptions depends, as is supposed by those who live in the neighbourhood of the geysers,

* This experiment proved unsuccessful in measuring the amount of pressure, although it enabled us to determine the temperature at the base of the geyser during the eruption. At Strokkr I was, however, successful in carrying out this experiment, but omit any detailed account of it, owing to the minute description of the apparatus employed, which would be necessary.

† I omit all further account of this subject, as M. Descloizeaux has given the numerical results of our combined observations on the periodicity of these phenomena during our sojourn at the geyser from the 3rd to the 14th of July.

‡ The temperature of the water at the surface of the basin of the geyser varied, during the time of the observations, from 76° C to 89° C.

on meteorological influences, an investigation into these conditions, although they are not as yet established as facts, and are unfortunately not within the scope of the researches of the passing traveller, would undoubtedly tend to confirm the theory whose principles I have attempted to develop.

If we compare this theory with the old hypothesis of the geysers, we can scarcely comprehend how the latter could maintain so long a place in the domain of science, since it is impossible to disregard the evidence contradicting it, furnished by the facts observed at every eruption. The idea involved in this hypothesis of subterranean cauldrons of vapour, supposed to be alternately filled with vapour and with water, is totally irreconcilable with the simple observation, that the masses of water propelled during the eruption beyond the margin of the basin, correspond perfectly with the depression of level that immediately follows, and, consequently, the supposed retreat of the water into an imaginary subterranean cauldron of vapour can have no reality. It would seem almost superfluous to mention another circumstance which shows the utter fallacy of this hypothesis, if it were not to prove more fully, that the lower part of the geyser frequently takes no part in the violent commotion manifested during an eruption at its upper portion. I have succeeded, during an eruption that attained a height of upwards of 43·3 metres, in keeping a thermometrograph uninjured in the lower part of the geyser tube by a manometer, and observing by this means, immediately before the eruption, a temperature lower by 9° C. than that which would correspond with the boiling-point at this spot. An observation that would involve an absolute absurdity, if, in accordance with the old hypothesis, we assume the eruption to be occasioned by boiling water being forced into the tube of the geyser from the depths below it.

The Strokkr, the greatest source of eruption in Iceland, next to the Geyser, is only a few hundred paces distant from it. The form of this spring presents peculiarities which must exercise a special influence on its mechanical results. Fig. 3, Plate II., gives a section of the tube of this spring as observed by the soundings instituted by M. Descloizeaux and myself. The tube is only $13^{m}55$ in depth, and not cylindrical as in the

case of the Great Geyser, but rather funnel-shaped, so that the diameter at the mouth is 2^m4, whilst it is only 0^m26 at a depth of 8^m3. The water, which rises to about 3^m, or 4^m5 from the mouth, has no means of escape, and is only expelled by the action of the eruption. As the column of water accessible to the sounding line is in a constant state of violent ebullition, the different temperatures must remain constant, and correspond with the pressure upon each stratum. In the following measurements, which were made by M. Descloizeaux and myself with every care and precaution, the time intervening since the last eruption has not been taken into account.

Height from the Bottom.	Temperature.	Height of Water-column corresponding with Pressure observed.
0·00 meters	115·0° C	(Eruption)
0·35 „	113·9° „	15·6 meters
2·95 „	114·2° „	15·1 „
4·65 „	113·7° „	15·6 „
6·20 „	109·3° „	13·6 „
8·80 „	99·0° „	10·2 „

From these experiments it follows:—

1. That the boiling-point of the strata of water in the upper and broader portion of the tube of the Strokkr corresponds precisely, as is required by the theory already developed, with the pressure acting on it.

2. That in the lower and narrower part of the tube, from the bottom to a height of 4^m6, the temperature remains the same (excepting very small oscillations).

3. That the temperature, amounting to 114° C., which remains invariable over a space of about 4^m6, corresponds to the boiling-point of a mass of water under a pressure of a column of water 16^m5 in height.

4. That, if we assume the lower and narrower part of the the channel to be filled with vapour to a height of 4^m65, as was the case at the time these measurements of the pressure were made, the weight of water acting on this vapour will actually amount to about 16^m5, or, at any rate, 15^m5.

5. That during an eruption ranging to a height of 48·7 met. the temperature at the bottom of the narrow canal rose to 115° C.

We cannot, therefore, doubt, that the lower and narrower part of the funnel of the Strokkr is filled by a column of steam, which regulates the uniform temperature of this part at different elevations, whilst the water, upheaved into the upper part of the funnel by the force of this vapour, is constantly kept in a state of ebullition.

The seat of the activity by which the great periodic eruptions are regulated, must be situated at depths inaccessible to direct experiment. This may easily be conjectured from the fact, that if the passage for the vapour be filled up with stones and earth, an eruption takes place from 20 to 30 minutes afterwards, by which all the impediments to the passage are expelled, accompanied by jets of muddy water, and when these have been wholly erupted, spouts of clear water are ejected, which not unfrequently measure upwards of 57 met. in height. It will be easily understood, that these eruptions breaking forth from that part of the steam channel which is alone accessible to our measurements, might be brought into a state of periodical activity, by a process similar to the mechanism of the Geyser.

Besides these periodic jets, whose prototype must be sought in the Great Geyser, and in the Strokkr Geyser, there is another species of intermittent thermal springs, whose activity is not manifested by the sudden occurrence of subterranean detonations of vapour, and whose eruptions are not characterised by sudden and rapid expulsions of boiling water. The *Litli Geyser* (Little Geyser) which belongs to the thermal group of Reykir, furnishes one of the most remarkable examples of the species. This spring rises in a palagonite rock, and is the highest but one toward the north-eastern mountain wall, at the foot of which rest the extensive siliceous tuff deposits of Reykir. A conical tuff elevation is here observed, whose small thermal crater is enclosed by stones. The boiling spout shoots forth periodically from among these stones, which are frequently not covered with the water, and exhibit, moreover, a very inconsiderable development of aqueous vapour. The eruptions were repeated very regularly at intervals of $3^h\ 45^m$ on the 24th and 25th of June, 1846, when I had the opportunity of observing the spring; the main eruption which occurred between 9 and 10 each morning, far surpassed the others in

magnitude and beauty. The approach of an eruption is made known by a gradual increase in the development of gas, and by a subterranean splashing sound. Boiling foam bursts forth with the vapours, and continues to rise and fall at slow intervals, until at length, after about 10 minutes, when the eruption has attained its maximum intensity, it rises in vertically and laterally spouting jets to a height of 30 or 40 feet. The waterspouts then decrease in height and circumference with the same gradations that marked their development, until the spring, at the end of about 10 minutes, returns to its former repose. This phenomenon is certainly inferior in magnitude to that of the eruptions of the Great Geyser in which a jet of boiling water, upwards of 28 feet in circumference, and 100 feet in height, sends its far projecting point of foam against the clear sky—but in beauty it is scarcely inferior to its colossal rival. The deafening hissing and roaring that accompany the eruption of the jets of water from the crater of the springs, in which one may distinctly hear the rushing of the masses of water, which fall down in torrents and are beaten to foam by the force of the vapours—the dazzling rainbows, which are formed with varying brilliancy from the reflection of the solar rays amid the pearly drops of the rushing cascades, and as rapidly disappear beneath the overwhelming mass of vapours—the dense and spherical vapoury clouds, which rising from the waterspouts, are made the sport of the winds as they stand forth in bold relief from the dark wall of rock behind them—the faint halo round the head of the colossal shadow which the traveller sees flitting across the clouds, and which, invisible to his companions, is seen by him alone. All these combine to excite in the mind of the traveller an indescribable impression of sublime grandeur.

We shall readily perceive that this spring cannot be maintained in a state of activity by the same causes that give rise to the eruption of the Great Geyser, if we consider the duration of its eruptions, their slow but regular increase and decrease, and the great regularity of their periodicity. All these phenomena appear, on the contrary, to be in perfect harmony with the hypothesis first advanced by Mackenzie, and since more widely extended by many others, regarding the existence of a subterranean cauldron or focus of vapour, which, as I have endea-

voured, I hope successfully to show, has been very incorrectly used in explanation of the eruptions of the Great Geyser. This hypothesis would appear to be applicable to the Little Geyser and the great number of similar springs found in Iceland. As, however, it would be foreign to the object of the present memoir to enter into the consideration of views, which it must be assumed are already known to the reader, and the importance of which will not be allowed until they can be proved by direct experiment, I will turn at once to another form of siliceous springs, which designate, as it were, the last stage of these formations.

I have already shown how the incrusting thermal springs of high temperature provide themselves in the course of centuries with a geyser apparatus, and thus necessarily pass into the condition of a continuous and intermittent source of eruption. The history of the development of these phenomena is not, however, terminated by this occurrence. The formations of siliceous tuff advance continually, until the apparatus of the geyser and the surrounding ground attain a height that must put an end to the eruptive activity of the spring, owing to the change effected in the relation of the height of the column of water and the heat evolved from the ground. As soon as the supply of heat from below, and the cooling at the surface, are so far in equilibrium, that the temperature of the mass of water is not anywhere able to reach the boiling-point, the action of the spring ceases spontaneously. Large reservoirs of tuff filled with hot stagnating or running water are then formed, whose depth and configuration depend upon the accidental condition of the margins, stalactitic formations, and the sinking in of the surface; all of which again depend to a great extent on the masses of palagonite that are continually brought to the surface in the form of soluble salts and silica by the water from subterranean depths.

Where such springs broke forth from deep points, they entirely disappear from their original positions, owing to the constant increase of the hydrostatic pressure to which they are subject, or only exhibit traces of their former activity in the disintegrated cavities of their vast siliceous tuff deposits, in which thermal activity is nearly, or wholly extinct. Among

the many instances that might be advanced in illustration of such changes, I will only mention the district of the Great Geyser.

The vast deposits of siliceous tuff with scarcely a trace of hot springs, which skirt the heights of the Bjarnafell, indicate an earlier condition of this stupendous thermal activity, that must have passed through the last period of development characterising these phenomena before they wholly disappear from the scene of their activity. Further downwards, but above the thermal region which is now in full activity, there are several reservoirs filled with hot water, in the depths of which the older geyser mouths may still be seen through the continually increasing deposits of silica which have accumulated in the course of ages. These springs, which recur in many parts of Iceland, and are especially remarkable at Reykir, are characterised by extreme beauty. In the depths of the clear unruffled blue waters of these basins, from which rises a light vapour, the dark outlines of what once formed the mouth of a geyser may be faintly traced amid the fantastic forms of the white stalactite walls. Nowhere can the beautiful greenish blue tint of water be seen in greater purity than in these springs.

A few remarks on the causes from which they are derived will hardly be superfluous.

Chemically pure water is not colourless, as is usually supposed, but naturally possesses a pure bluish tint, which is only rendered visible to the eye when the light penetrates through a stratum of water of considerable depth. That such is the fact may easily be shown by taking a glass tube, 2 inches wide and 2 metres long, which has been blackened internally with lamp-black and wax to within half an inch of the end, the latter being closed by a cork. Throw a few pieces of white porcelain into this tube, which, after being filled with chemically pure water, must be set vertically on a white plate, and looking through the column of water (of two metres) at the pieces of porcelain, which can only be illumined from below by white light, we shall observe that the objects will, under these circumstances, acquire a pure blue tint, the intensity of which will diminish in proportion as the column of water is shortened,

so that the shade of colour becomes at length too faint to be perceived. This blue coloration may also be recognised when a white object is illuminated through the column of water by sunlight, and seen at the bottom of the tube through a small lateral opening in the black coating. The blue tint so frequently observed in water cannot, therefore, be regarded as in any way strange. The question rather arises, why this blue colour is not seen everywhere, and why it should not occur in many seas? why, for instance, the lakes of Switzerland, the waters of the geysers in Iceland, and in the South Sea Islands, should exhibit every shade of green, whilst the waters of the Mediterranean and Adriatic are occasionally of so deep a blue as to vie with indigo? These questions are easily answered, since clearness and depth are the primary if not the sole requirements for imparting to water its natural colour. Where these fail, the blue tint will likewise be wanting. The smallest quantity of coloured elements which the water may take from the sand or mud of its bottom, the smallest quantity of humus held in solution, the reflection of a dark and strongly coloured bottom, are all sufficient to disguise or alter the colour of water. It is well known, that the yellowish red colour of the waters which traverse the lower group of the trias formations depends upon hydrated oxide of iron, contained in the mud of the variegated sandstone. From a similar cause, the vast glacier streams of Iceland, which, in these desolate regions where there are neither roads nor bridges, the traveller finds, to his discomfort, that he must ford—are rendered opaque and milk-white from the detritus of dark volcanic rocks, which, crushed into a white powder by the overwhelming mass of the descending glaciers, are carried to the sea, in the form of white mud and sand, and again deposited there in vast deltas.

In like manner, the natural colour of the small lakes in the marshy districts of Northern Germany is concealed by the black tint imparted by the dissolved humus derived from the turf. These waters often appear brownish or black, like the water in most of the craters of the Eifel and Auvergne, where the sombre volcanic rocks obstruct the reflection of the incident light. It will, therefore, easily be understood that it is only

where these disturbing influences do not exist that the colour of the water will be seen in all its beauty. Amongst the places at which this requirement is most completely fulfilled, we may especially instance the Blue Grotto at Capri, in the Gulf of Naples. The sea is there most remarkably clear to a very great depth, so that the smallest objects may be distinctly seen on the light bottom at a depth of several hundred feet. All the light that enters the grotto, the entrance of which is only a few feet above the level of the sea, in the precipitous rock opening upon the surface of the water, must penetrate the whole depth of the sea, probably several hundred feet, before it can be reflected into the grotto from the clear bottom. The light acquires, by these means, so deep a blue coloration from the vast strata of water through which it has passed, that the dark walls of the cavern are illumined by a pure blue radiance, and the most differently coloured objects below the surface of the water are made to appear bright blue.

An equally remarkable example of this fact presents itself in the glaciers of Iceland as well as in those of Switzerland, which shows that water does not lose its original colour even when in a solid condition. At the distance of many miles, the eye may distinguish, on the flat heights of the "Jokull," the boundaries that separate the bluish ice of the glaciers from the white inaccessible plains of snow that rise to the summit of these mountains. On a closer examination of these glaciers, one is surprised to observe the purity and transparency of the ice, which often appears to be wholly free in large masses from vesicles of air and foreign admixtures, whilst its vast fissures and cavities are coloured all shades, from the lightest to the darkest blue, according to the thickness of the strata through which the light has penetrated.

The blue tint of the cloudless and vapoury atmosphere is probably dependent on similar phenomena, if we are justified in concluding, from the colour of solid and fluid water, that aqueous vapour has a similar colour. On considering all these facts, we can scarcely doubt for a moment that the blue colour of water is a peculiar and not accidental characteristic of that substance. This natural colour of water will also afford us an easy explanation of a light green tint which is even more

strongly manifested in the crystal-like siliceous springs of Iceland than in the lakes of Switzerland; for the yellow colour derived from traces of hydrated oxide of iron, in the siliceous sinter walls surrounding the water, blends with the original blue to produce the same greenish tint, which, in the Swiss lakes, is derived from the yellow bottom;—the most different rocks experiencing a superficial decomposition from the continued action of water, and becoming tinged with yellow by the formation of hydrated oxide of iron. Hence it will be easily conceived that the blue, which continues to increase in intensity with the increased depth of the strata of water, may obliterate the action of this yellow reflection, and thus either weaken, or wholly destroy, this greenish tint. The green grotto on the shores of Capri affords a most striking proof of this fact. The green colour, which is produced by the reflection, at an inconsiderable depth of water, from the yellowish limestone constituting the bottom and the walls of the grotto, illuminated by the light from without, wholly disappears in the enormous depths of the water of the blue grotto; there a pure blue colour takes the place of the green, observed in the shallower cavern, although the water and rocks are the same in both cases.

We have already shown, that these siliceous thermal springs, having so high a temperature, combine all the requirements necessary for passing through the various phases which characterize geyser formations. In order, therefore, fully to understand these phenomena it only remains to revert to the origin and the mode of formation of the alkaline siliceous springs, to which the deposits of siliceous tuff owe their origin. It will be necessary to start from some definite point, and I will, therefore, make choice of the water of the Great Geyser, whose composition corresponds in every essential point with that of all the other siliceous tuff springs of Iceland.

The analysis was made in my own laboratory by Dr. Sandberger, from a specimen which I took from the basin of the geyser immediately after an eruption in the beginning of July, 1846. As Dr. Sandberger will himself give a more detailed account of his experiments, I will limit myself to a mention of the results of his analysis, the accuracy of which I had several opportunities of testing. I subjoin the analysis lately

made by Damour of the same water, in order that my readers may compare the two.

Water of the Great Geyser.

	Sandberger.	Damour.
Silica	0·5097	0·5190
Carbonate of soda	0·1939	0·2567
Carbonate of ammonia*	0·0083	....
Sulphate of soda	0·1070	0·1342
Sulphate of potash	0·0475	0·0180
Sulphate of magnesia	0·0042	0·0091
Chloride of sodium	0·2521	0·2379
Sulphide of sodium	0·0088	0·0088
Carbonic acid	0·0557	0·0468
Water	....	998·7695
	1000·0000	1000·0000

In a letter to Berzelius, dated 3rd of November, 1846, and which has been partly published in the German Journals, I have given a short notice of the results of my experiments and observations on the origin of the Icelandic thermal springs, from which I make the following extract:

"An investigation of the phenomena of the springs at the place of their origin readily leads the observer to the conviction, that the same chemical activity, by which the scene of these stupendous natural phenomena is characterised, must have played an important part in the formative process of older rocks. As a general fact it may be admitted that none of the rocks of which the island is formed, resists the decomposing action of the thermal waters. Wherever these waters break forth, whether in a liquid or vaporous form, whether in the most ancient structures of the island, as in palagonite tuff, or in clinkstone and trachyte, the next in order of succession,—in the older trap, which has been thrown out in veins after the clinkstone period, and has spread through the tuff, forming vast strata,—in the basaltic eruptions which followed the last-named period,—or, finally, in the most recent lava

* The ammonia was obtained by adding recently heated hydrate of potash, and distilling the water into a receiver containing hydrochloric acid; the last having previously been purified from all admixture with ammonia, by being distilled with chloride of platinum. The portion of water analyzed was brought from Iceland in a glass tube hermetically closed.

eruptions, a decomposition may everywhere be observed, which, agreeing in its fundamental type, has probably, under the co-operation of secondary influences, given rise to all the various products which are found in the craters of Hecla and Kraffa, as well as in the vicinity of the Great Geyser and the different suffiones.

"The different siliceous compounds formed at the bottom of the springs are converted by the action of the thermal water into acid and basic silicates. The former are dissolved by the water, whilst the latter constitute an insoluble stratum of clay, whose gradual transition into the original rock may be clearly traced at certain points, but more especially at the confines of the fumerole activity. The distribution and size of these secondary argillaceous strata stand in direct relation to the magnitude of the thermal phenomena, and with the temperature of the water, which, at a considerable depth, is not unfrequently upwards of 100° C. The soluble silicates which proceed from these fissures are brought to the surface with the thermal water, giving rise, where it is left to evaporate freely to the formation of siliceous sinters and opals.

"Two gases, namely, sulphuretted hydrogen and sulphurous acid, occur together with sulphur, as the important accompaniments of these vapour and boiling springs; and impart a somewhat different character to these simple processes, by calling forth a series of secondary products."

Subsequently to the period when the above was written, M. Damour has made known (in the *Annales de Chimie et de Physique*, 1847,) that heated mesotype is partially dissolved by boiling water, silicate of soda being formed; and he thus furnishes us with a very interesting addition to the above remarks. Amongst the rocks which I have indicated as subject to this decomposition, palagonite occupies the principal place. The geognostic relations of the Great Geyser (the largest source of siliceous tuff in Iceland), which lies at the foot of an erupted trachytic clinkstone, appear to indicate the existence of a special connexion between these rocks and the siliceous tuff deposits, and such has been supposed by Damour to be the case, but, independently of the circumstances, that other springs of this kind, as those lying on the north-west of Hecla

at the foot of the Randakamba, standing in precisely similar relations to the clinkstone, are by no means characterised by their siliceous tuff formations, it may be also determined with certainty from the secondary decompositions of the bottom of the spring, that it consists of palagonite tuff, which exercises the most essential influence on the formation of the geysers.

In order to show the truth of these facts, it will be necessary to enter somewhat more fully into the consideration of the decompositions experienced in palagonite by the action of hot water, carbonic acid, and sulphuretted hydrogen. On digesting pulverised palagonite in a strong and closely corked glass vessel with distilled water for some hours, at a heat of 100° or 106° C., silicic acid, potash, and soda are dissolved. 1000 grammes of water after 12 hours' digestion yield, in this manner, a solution containing the following proportions:—

Silica	0·03716
Soda	0·00824
Potash	0·00162
	0·01702 gram.

On allowing water, saturated with carbonic acid, to act on the pulverised mineral, all the constituents, with the exception of alumina and oxide of iron, will be dissolved in the form of bi-carbonates. 1000 grammes of this water, after four hours' digestion, yielded the following constituents:—

Silica	0·09544
Bi-carbonate of lime	0·16893
„ magnesia	0·05333
„ soda	0·06299
„ potash	0·00189
	0·38268 gram.

On heating pulverised palagonite in a similar manner, for ten hours, in water saturated with sulphuretted hydrogen, sulphide of iron was formed, and the solution contained, for 1000 grammes, the following constituents:—

Silica	0·1175
Sulphide of calcium	0·2748
„ magnesium	0·0727
„ sodium	0·0438
„ potassium	0·0410
	0·5498 gram.

We see from the relations existing among these salts themselves and with the silica, that the constituents of palagonite take very different parts in the decomposition which is induced by hot water, carbonic acid, and sulphuretted hydrogen respectively; whilst, as we have already seen, this mineral is entirely dissolved in hydrochloric and sulphurous acids, except a small quantity of silica left as a residue. The alkaline siliceous springs, in which there is a smaller quantity of this volcanic gas, assume, consequently, a very different character from the waters of the suffiones; since it is evident, that the composition of the water, and the nature of the argillaceous deposits produced from these actions, must stand in a definite relation to the greater or smaller resistance opposed by the separate constituents of palagonite to the action of the weaker volcanic acids, that is to say, to the water, carbonic acid, and sulphuretted hydrogen gas. I must reserve the further development of the relation in which the clay of the geyser stands to the constituents of the water of the geyser; since the necessary data can only be attained by an examination of the residuary matters left by palagonite, after the long-continued action of water, carbonic acid, and sulphuretted hydrogen.

I think I may, however, pass over the last relations, since the results already obtained by a decomposition of palagonite are sufficient to give an explanation of those processes, to which the constituents of the alkaline siliceous springs owe their origin; and which, moreover, manifest themselves as the original causes of all the phenomena presented in the different phases of the development of geyser formations.

When the alkaline silicates, removed by the heated water from the palagonite, are brought into contact with carbonic, hydrochloric, and sulphurous acids, (the latter of which is formed by the oxidation of the sulphurous acid through the oxide of iron in the palagonite,) these alkalies must be converted into carbonates, sulphates, and chlorides, whilst the silicic acid remains dissolved in the alkaline carbonates and in the water, and is partially separated from them, by evaporation, as siliceous tuff,—a fact already observed by Black, in 1792.

The action of the carbonic acid is not, however, limited to the alkalies taken up by the water, but is directly extended,

as may be seen in our second analysis, to the substance of the palagonite, since it not only gives rise to a solution of silica in water and alkaline carbonates, but also forms acid carbonates of magnesia and lime. The fact that only traces of the first named of these earths are found in the geyser water, may be easily explained from the circumstance, that the acid carbonate of lime is decomposed by boiling into carbonic acid and an insoluble neutral salt, or is decomposed in the same manner by the alkaline silicates, whilst an alkaline carbonate is formed. Magnesian salts, on the other hand, whose solution, when very much diluted, undergoes, as is well known, only an incomplete precipitation, must, therefore, in accordance with the analysis, occur in traces in the water of the geysers.

The products of sulphuretted hydrogen on palagonite, which, as I have before observed, furnish the key to an explanation of the formation of pyrites in the clay of the geysers and fumeroles, experience a similar decomposition by carbonic acid. Sulphuretted hydrogen, which is never absent from the thermal limits of the geysers, escapes as a gas, whilst carbonate of lime and, to a certain degree, carbonate of magnesia are precipitated. The ultimate product of these reactions is silicic acid dissolved in water and alkaline carbonates, to which alkaline sulphides, as the constant accompaniments of these siliceous springs, are added, when the carbonic acid forms a less strongly characterised constituent. We here meet with a simple explanation of the origin of siliceous sinters.

The relation of the potash to the soda in the geyser water is totally different from that which exists in palagonite. The quantity of the former is most strikingly inferior to that of the latter in almost all these waters. Although, in the above analysis, the quantity of the constituents sought is too small, and the duration of the decomposition of palagonite much too short, to lead to an accurate determination of the relation of the bases to silicic acid, we yet can find that the soda is dissolved from palagonite by pure water, or carbonic acid, in a much larger proportion than the potash; and even in a much larger relation, by the carbonic acid, than corresponds to the composition of the geyser water. We may, therefore, easily understand that when the three volcanic gases are simul-

taneously exercising a decomposing influence, these alkalies may easily be dissolved to the relative extent in which they occur in the waters of the geyser.

I have already remarked that all the volcanic rocks of Iceland experience, under the influence of water and volcanic gases, a similar although much slower decomposition than palagonite. This is most strikingly observed in the volcanic incorporations of the palagonite tuff, which are gradually, although slowly and with difficulty affected by the decomposing action of the fumeroles. On comparing the quantity of the argillaceous layer produced by the decomposition of the palagonite tuff with the extent of the contiguous siliceous tuff formations, it will be evident that they stand in a mutually controlling relation to one another, and that it is especially palagonite which constitutes the peculiarity of Icelandic thermal phenomena. I think, I may even venture to assert, that geyser and siliceous tuff springs (all other conditions being the same) are connected with the occurrence of palagonite tuff, or with structures similar to palagonite.

If I may be permitted, I will conclude the present memoir (in which I have collected some of the data of a larger work on which I am at present engaged) by extracting a few general considerations from the letter to Berzelius to which I have already alluded.

A careful study of the actions of fumeroles, as it may be observed on so large a scale in the fissures which maintain the connexion existing between the focus of volcanic forces and atmospheric phenomena in Iceland, leads us imperceptibly back to the theatre of that great volcanic catastrophe, by which the trap was upheaved through the tuff and clinkstone rocks, and distributed in vast strata through them.

I will here only speak of a few facts which may be classed amongst the most common in Iceland. Where the clinkstone and older trap break through the tuff, and still more, where the older trap penetrates in veins through the clinkstone, the penetrated rock exhibits a fused and disintegrated appearance, by which it assumes characteristics resembling those of obsidian or pitch-stone. On tracing the horizontal strata which have been erupted from these veins, at their points of contact with the

tuff, we soon lose sight of all appearance of fusion or the action of fire. On examining the tuff more carefully, we are astonished to discover that the main body of it is composed of an easily fusible hydrated silicate, which has preserved its original character and its normal proportion of water, notwithstanding its immediate contact with vast strata of trap which have penetrated in a glowing and fused condition. Still more singular are the innumerable vesicular cavities in the amygdaloid alternating with the tuff and trap, which are lined and not unfrequently completely filled up with quartz, chalcedony, calc-spar, zeolites and other hydrated silicates.

How could these hydrated compounds have arisen from plutonic mineral masses, closely invested by glowing hot trap, or how could they be preserved unchanged?

These questions are explained by the phenomena of the present active fumeroles. So porous a structure as tuff must necessarily be penetrated by moisture throughout its entire mass, and thus be filled with strata and currents of water, which must have given rise to the phenomena, which appear at first sight so inexplicable, since the great catastrophe of the elevation of trap was of a subsequent date. Where the hot fluid trap came in contact with an inconsiderable cooling surface, as at the mouth of the vein, the water has yielded and been expelled by the action of the constantly renewed stream of fire, which would then prove more than sufficient to fuse the anhydrous rock. On the other hand, where the fluid rock spread out from these veins in far extended horizontal strata, and penetrated through the upheaved tuff, the further development of the igneous action on the surrounding rock must have been arrested by the increased production of aqueous vapour; the great specific heat of the water and the considerable latent heat of its vapour, making a greater elevation of temperature impossible in the tuff strata. The magnitude and extent of these igneous actions, at considerable distances from the veins, stand in a direct relation to the preponderance of the trap strata over the tuff deposits.

If this view be correct, the fumerole actions, which are owing to the vast development of aqueous vapour, must necessarily be found to occur in the tuff and trap masses which

served as a focus for their activity. Appearances fully corroborate these views. For the amygdaloid which is so rich in hydrated silicates, and alternates with tuff and trap, presents a faithful picture of the phenomena of decomposition which may still be met with in full activity in the Icelandic suffiones and thermal springs. In these vast amygdaloid rocks, which present the mineralogist with one of the richest and most interesting sources of mineral species, we may easily recognise the origin of the metamorphosis of the rock, which occurs at the points of contact between the trap and the tuff strata. Their principal mass consists of a ferruginous or siliceous clay, which occurs as a product of fumeroles still active, and after passing through innumerable phases of decomposition merges into the perfectly undecomposed strata of both these species of rock. Pyrites, chalcedonous quartz, and opal, which are so characteristic of fumerole structures, are scarcely ever absent, whilst everything justifies the assumption, that this remarkable penetration of aqueous and plutonic formations is to be ascribed to a great manifestation of fumerole activity which has immediately followed the catastrophe of eruption; the original rock being converted into aluminous amygdaloid, by a separation of its constituents, into soluble and insoluble silicates, in a manner analogous to what may still be observed. By these means, the plastic clay might easily be filled, through the agency of vapours and gases, with those innumerable vesicular cavities in which the products of crystallization of the soluble silicates which penetrate the clay are traced as supplementary constituent parts. Whether I shall succeed with the materials at my command in explaining the local conditions, on which the formation of the various silicates depends, is a question that can only be decided by an experimental investigation, at the place and focus of the phenomena treated of in these observations.

The relations of superposition of the Doubly refracting Iceland spar, which have been so carefully investigated by M. Descloizeaux, and which appear so inexplicable on a first examination, can easily be explained by considering the fumerole actions from the above point of view. In like manner all the difficulties attending the explanation of the recent and unexpected discovery of the occurrence of petrified infusoriæ in the decomposing crust

of volcanic rocks, may easily be explained when we consider that the mass of such structures, converted by fumerole action into clay at its surface, and then subsequently solidified by the infiltration of soluble silicates, might easily contain within itself the conditions necessary for the preservation of the microscopic organisms, whose petrified remains are still found within these strata.

THE END.

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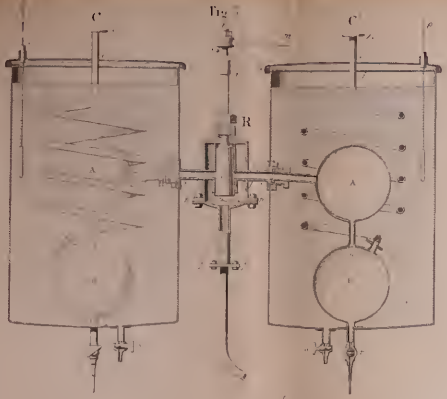


Fig 3

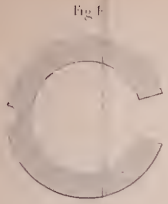


Fig 4

Fig 1

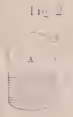
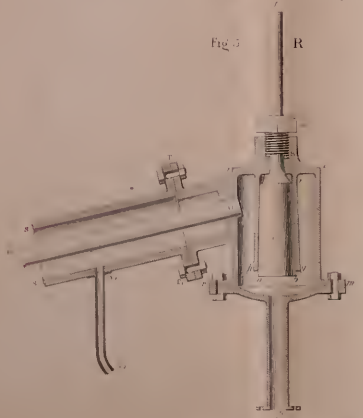


Fig 2



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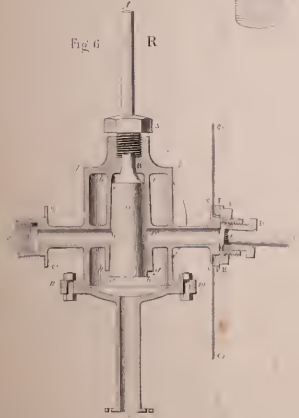


Fig 6

Fig 7

Scale of Figures 3 & 4

Scale of Figures 5 & 6

Fig. 1

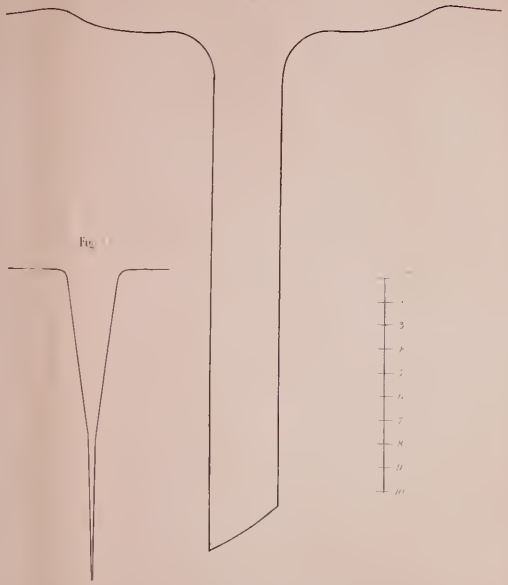
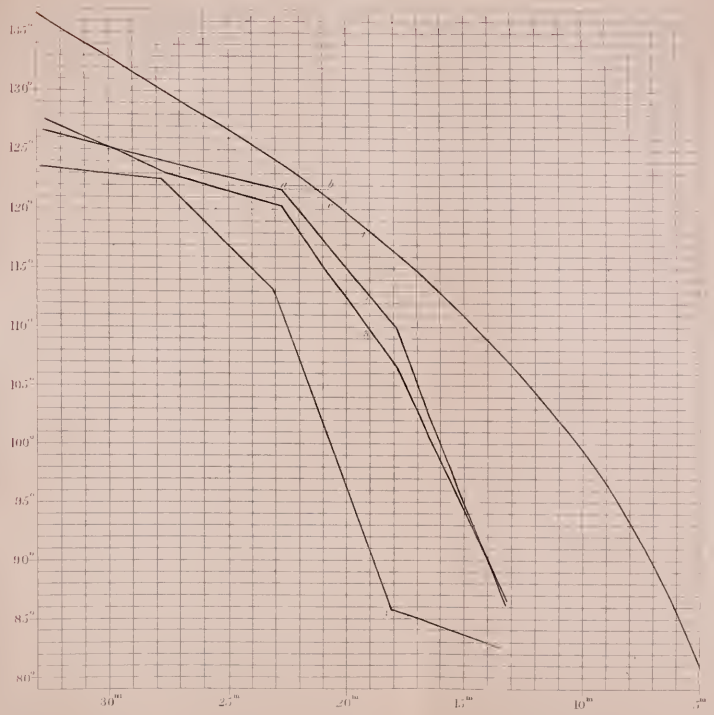


Fig. 3

Fig. 2



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